Vol. 1 SEPTEMBER, 1918 No. 9

Journal

—OF THE—

American Ceramic Society

A Monthly Journal devoted to the Arts and Sciences Related to the Silicate Industries.

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Published Monthly by the
AMERICAN CERAMIC SOCIETY

Publication Office
211 Church St., Easton, Pa.

Editorial Office
Rutgers College, New Brunswick, N. J.

SIX DOLLARS PER YEAR (Foreign Postage Additional) *SINGLE NUMBERS, SIXTY CENTS*

Entered as second-class matter, July 15, 1918, at the post office at Easton, Pa., under the Act of March 3, 1879.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized August 16, 1918.

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JOURNAL
OF THE
AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1 **September, 1918** **No. 9**

EDITORIALS.

THE PATENT SITUATION.

A mode of relaxation available to any ceramist is the study of current patent specifications referring to inventions of a ceramic nature and which is certain to afford a constant source of amusement. Still, a feeling of apprehension is apt to creep over the unsophisticated follower of the fictile arts when he discovers that he is daily and unsuspectingly violating valuable privileges by making use of the common constituents of his products. For, have not patents been issued upon the employment of kaolin, feldspar and quartz in ceramic bodies? Indeed, this is not a jest but the solemn truth as may be readily proven by reference to the official lists. And what of the weird compositions of glasses, enamels and glazes to say nothing of the wonderful compositions of refractories, cement brick and other products which have been duly protected. Equally elevating is the perusal of the patent descriptions referring to kilns, driers, furnaces and other appliances employed in our art, some of which represent ideas hoary with antiquity.

Seriously speaking, the situation as regards ceramic patents is appalling. It is evident that our whole system of affording patent protection to inventions relating to our industries is without rhyme or reason. Like heaven's mercy, patents fall both upon the just and the unjust and the result is injustice and chaos.

So much has already been written on the general deficiencies of our patent system that it seems futile to join in the chorus, but the situation is so grotesque when applied to the silicate industries that it is our duty to raise our voice in protest.

Such a complaint is the more justified when one considers that the remedy is neither difficult nor complex. The creation of a small committee of experts for each of the natural divisions of industry and technology, among them one for the field of ceramics, would bring about the desired change, namely, full protection of original ideas and rejection of the undeserving claims. By making the experts responsible to the Government in their oath of office, there is every reason to believe that under the guidance of the regular officials the work would be well and efficiently done.

It would be folly to place the blame for the present conditions upon the hard-working examiners of the patent office. It was not intended that they should be omniscient and they are doing the best they can. However, when so many things are being changed for the better these days it is our devout hope that something be done in the matter of our patent system.

PROFESSIONAL DIVISIONS.

It would appear that in the "Professional and Industrial Division" idea, there lie great possibilities for a broader and more useful activity and permanent growth of the American Ceramic Society. Carefully and successfully worked out, it will remove the greatest barrier to growth in membership with which the Society has had to contend in the past, namely: indifference of members, especially the practical man, to regularly attend meetings at considerable expenditure of time and money when 90 per cent of the program is either "high brow stuff" passing way over his head, or else devoted to an industry having nothing akin to his own.

In order to secure the fullest exchange of views on mutual problems, the confréres must feel at ease, which is certainly not the case when the average man gets on his feet to discuss a paper in a regular meeting, with the stenographer interrupting in about the middle of the second sentence to ask his name and the man himself realizing that if he should happen to use the word "about" or "approximately" someone would be sure to pop up the minute he was through and "object to the use of the word 'about' on the floor of this Society, etc." Everyone who has ever attended

the Society meetings knows that time and again points are raised which certain men in the room could and would gladly clear up were it not for a reluctance they feel in rising to their feet under the conditions which usually prevail at our general meetings.

Industrial Divisions will do away with this to a large extent. Members in the same or allied industries will gain the confidence of and learn to know each other better and great good will result. Of course, it is not to be presumed that the general meetings will be entirely superseded by the Division meetings, but rather that a portion of the time will be set aside for the latter purpose. If the Industrial Divisions could continue to hold periodic meetings throughout the year, so much the better, but even if the Division meetings are confined to two each year, at the annual and summer meetings, they will justify their organization.

THE GLASS INDUSTRY.

The desirability of securing the more active coöperation of the glass industry with the American Ceramic Society has been repeatedly emphasized. The rapid progress which has been made in this country during the past four years in the technical advancement of certain branches of this industry should serve to awaken the interest of the other branches in a representative technical organization such as the American Ceramic Society.

The Society has been fortunate in securing a gratifying number of excellent papers on glass for publication in the numbers of the Journal issued thus far and in receiving the assurance of an adequate supply of papers of interest to glass technologists for the future numbers.

Particular attention is called to the fact that the present number includes three excellent papers of both practical and technical value to those engaged in the glass industry. It is to be hoped that our members will bring this number to the attention of their friends and acquaintances who have not as yet become actively interested in the Society.

ORIGINAL PAPERS AND DISCUSSIONS.

THE IDENTIFICATION OF "STONES" IN GLASS.

By N. L. Bowen.

Introduction.

In glasses intended for a great variety of uses, and particularly those for use in optical instruments, homogeneity is a principal requirement. It is one of the tasks of the glass-maker, therefore, to eliminate foreign particles and inhomogeneity of any kind in such glasses. Foreign particles may be of a gaseous nature, when they are termed seeds, bubbles, blisters, etc. Foreign material may be of a vitreous nature, when it is described as tears, cords, striae, etc., and, finally, foreign particles of a crystalline nature are commonly called stones. Complete elimination of all of these is never attained in glass practice, with the result that selection of the product is usually necessary and the amount of acceptable material becomes a measure of the efficiency of the process of manufacture. In this paper attention is directed towards the occurrence of stones in glass, and particularly towards the information regarding the nature of stones that is to be gained through the use of the petrographic microscope. Since an exact knowledge of the nature of a defect in any material may be a fundamental factor in achieving its elimination, it is hoped that this study of stones in glass may be of some service to the glass-maker. It should be remarked that most of the stones examined by the writer were those encountered while he was engaged in the production of optical glass.

Varieties of Stones.

It has been the experience of glass-makers that a variety of factors may give rise to stones. A classification of stones according to their origin may be given as follows:

1. Pot stones
2. Batch stones
3. Crown drops
4. Devitrification stones

It is often a matter of great importance to a glass-maker, when his glass is running stony, to be able to refer the stones definitely to one of these four classes. If they are pot stones, *i. e.*, actual fragments of the pot, he must look for the trouble in his clays, in his treatment of the pots, in excessive temperature of his furnaces or in a particularly, and perhaps unnecessarily, corrosive glass batch. If they are batch stones, or residual batch material undissolved, he must look to the grinding and mixing of his batch materials, to a proper balance in the proportions of these materials, or to the possibility of too low a temperature at some stage of the melting process. If they are crown drops the grade of bricks used in the crown or the length of flame must be considered. If they are devitrification stones, formed by devitrification or crystallization of the glass after it has been completely melted, he must look to the rate of cooling or to an ill-chosen glass composition.

Identification of Stones.

Chemical analysis of stones is sometimes resorted to in order to determine what their origin may be, but it presents considerable difficulty. Stones are usually quite small so that the chemist must, as a rule, work with a small amount of material; indeed it is sometimes impossible to obtain an adequate amount. It is no easy matter to separate stones from the enclosing glass, so that he must work with contaminated material. As a result of these various factors a chemical examination may consume much time and even then may be unsatisfactory. Then again there are certain types of stones whose chemical composition alone may leave one in some doubt as to the class in which they should be placed. With the aid of the petrographic microscope, on the other hand, it is usually possible to determine rapidly and decisively the origin of a stone, since not only its mineral composition is determinable, but also its internal structure and its relations to the surrounding glass.

The best method of examining stones under the microscope is

to crush them to a powder and examine the powder in a drop of liquid on a slide after covering with a cover slip. With the aid of a set of liquids of various known refractive indices, the high and low indices of the crystals can be measured by the method of comparison and at the same time extinction angles, optic axial angles and other distinctive optical properties observed. The method is highly advantageous for fine materials intimately intergrown, because immersion in a liquid corresponding in index to one of the materials presents the other in marked relief and renders possible a study of the details of the manner of intergrowth.

Pot Stones.

Pot stones are occasionally large enough that when broken open they reveal their nature to the unaided eye. Usually they are quite small, however, and even when formed from pot material that burns very dark they are snow-white and in this respect indistinguishable from stones of different origin. Under the microscope, pot stones are found to be made up, in all cases, of crystals of sillimanite with a little interstitial glass. The sillimanite or aluminium silicate (Al_2SiO_5) is recognized by its usual crystallographic and optical properties identical with those of the natural mineral. Sillimanite is never found in stones of other origin.

It may be remarked in passing that this recrystallizing action of the glass on the pot material is operative not merely on fragments of the pot that have become detached, but also on the wall of the pot itself. The result in this case is the formation of a thin but conspicuous white layer on the inner surface of the pot that is made up of minute crystals of sillimanite with a little interstitial glass.[1] In attacking pot material the glass evidently acts selectively, dissolving first from the clays the portion of the silica in excess of that necessary to form sillimanite. All glasses act alike in this respect so that sillimanite is a universal constituent of pot stones and of the white layer formed on pots whatever may be the composition of the glass. As a result of this selective action of glass on clay material, the more silicious pots are much

[1] G. V. Wilson has examined this white layer and found it to contain crystals of sillimanite. See S. N. Jenkinson, *J. Soc. Glass Tech.*, **2**, No. 5, 14 (1918).

more vigorously attacked than the more aluminous varieties. This does not necessarily mean that the silicious pots give more stony glass, however, for the stones formed may be more readily assimilated by the glass. It is rather a lack of uniformity in pot material that is to be avoided, for this may give local pitting and the casting of highly resistant stones.

Having ascertained that stones have their origin in his pots, the glass-maker may then take such steps to remove them as naturally suggest themselves, such as more careful preheating of his pots, altering the glass batch to render it less corrosive, melting at lower temperature, and, of course, altering the pot batch.

Batch Stones.

The only normal constituent of a glass batch that is ever left unassimilated by the glass is the sand. It then occurs as whitish grains embedded in the glass and having the same general appearance as stones of any other type. Under the microscope batch stones are found to consist entirely of silica in one of its forms. Frequently there persists in the grain a core of the original quartz of the sand and this is surrounded by a layer of cristobalite or a mixture of cristobalite and tridymite. Occasionally a small grain may be altered entirely to cristobalite and tridymite, when the core is a dense mass of that material without interstitial glass, differing in this respect from these forms of silica when they occur in devitrification stones to be described later. These various forms of silica are readily recognized by their characteristic optical properties. Excessively fine-grained cristobalite and tridymite are not readily distinguished the one from the other, but this is often a matter of no great moment since the material is readily recognized as one of the low-refracting forms of silica.

A batch stone is usually surrounded by an aura of glass of lower refractive index than the glass as a whole and frequently there is a "tail" of similar material (see Fig. 1). These are the result of the gradual solution of the silica of the stone and are wholly lacking in the case of silica stones that originate through devitrification.

For the elimination of batch stones, the glass-maker should melt at a higher temperature or introduce more "fluxes" into the

batch, that is, he should proceed in a manner directly opposed in most respects to that required for the elimination of pot stones, wherefore the importance of distinguishing these two types of stones. There are, of course, other possible remedies for batch stones, such as the use of finer or more uniform sand, the careful mixing of batch ingredients, etc.

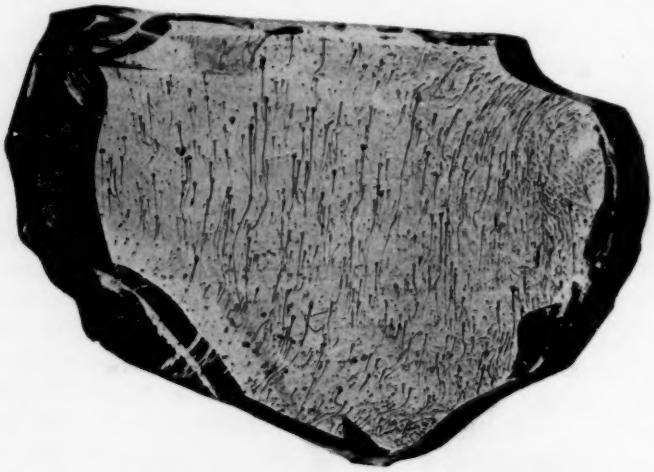

FIG. 1—Batch stones with tails. An extreme example.

Occasionally, through the careless handling of batch materials, they may acquire extraneous matter that is unassimilable by the glass and therefore appears as stones. Identification of such stones may sometimes be accomplished under the microscope and a clue as to source thereby obtained.

Crown Drops.

When the crown of a furnace becomes rather badly corroded by the vapors that are given off by glasses, some liquid may drip from the bricks of the crown and carry particles of the brick with it. Where silica bricks are used, as they commonly are in American practice, grains of silica are thus introduced into the metal and may persist in the finished product. At first thought it would seem that particles of silica added in this manner would differ in no particular from grains left over from the batch, but as a matter

of fact they usually can be distinguished. When quartz is acted on by fluxing materials it changes first to cristobalite, even at temperatures where tridymite is the stable phase, and then the cristobalite is gradually made over into tridymite. For this reason the silica of batch stones, which is fluxed in the glass for a comparatively short period, is predominantly cristobalite and usually very fine grained, for it is continually dissolving and has no opportunity to grow to large dimensions. The silica from the crown, however, has been fluxed for a long period in the liquid that forms on the surface of the bricks before it arrives at that state where drops are likely to form. In the writer's experience of both regenerative and blast furnaces, complete conversion to tridymite is accomplished in this surface material and rather large crystals have grown that are easily distinguished from the fine-grained cristobalite of batch stones. From furnaces whose crowns are maintained at temperatures above 1470° C for lengthy periods, which is rarely done in glass practice, cristobalite should be formed rather than tridymite, and Merwin describes cristobalite from the crown of a recuperative furnace.[1] In such a case the rule that crown drops are made up of tridymite would not hold, but even here it seems likely that the cristobalite would have grown to much larger dimensions than in batch stones and might be distinguished by this fact. Of course one can always determine, for any particular furnace, the exact nature of the material that would enter into the formation of crown drops by chipping off some of the glaze from the bricks of the crown when it is cold enough to render this possible.

Devitrification Stones.

Devitrification or crystallization of glass may make its appearance in various forms. When crystals are formed that are large enough to be seen as individuals with the unaided eye and are disseminated through a glass which is otherwise clear and transparent, they are usually described simply as crystals and the glass is said to have undergone "crystallization." When the crystals are small and closely spaced, so that the effect is to render

[1] Ferguson and Merwin, "The Melting Points of Cristobalite and Tridymite," *Am. J. Sci.*, [4] **16**, 424 (1918).

the glass an opaque white mass, the glass is said to have undergone "devitrification." There is, however, no essential difference and such difference as appears is simply the result of the limitations of the human eye. Under the microscope a piece of "devitrified" glass is seen to consist of a clear transparent glass base through which crystals are dotted, the whole appearance being the same as that presented to the unaided eye by a piece of glass that has undergone "crystallization," as that term is used above. While the formation of minute crystals in glass, in such manner that the whole mass is rendered opaque, can hardly be referred to as the formation of stones, it is, however, considered to some extent here since the phenomena are fundamentally the same. A common misconception concerning devitrification should, perhaps, be mentioned at this point. It is sometimes considered, when a piece of glass is rendered a dense opaque mass, that it has crystallized as a whole. This is far from the truth. Almost invariably there are formed crystals of only one of the compounds occurring in the glass and the crystals themselves seldom amount to more than 10 or 15 per cent of the total mass of glass.

A common form of crystallization or devitrification is that in which spheroidal masses of crystalline material are formed in the glass. These are analogous to the spherulites that occur in natural glasses, *i. e.*, volcanic lavas. In artificial glasses they are made up of innumerable minute crystals of one of the constituents of the glass radiating from a center and having glass in the interstices between the crystals or radii. These spherulites constitute the typical devitrification stones. Occasionally crystallization of this kind begins with the formation of a rather large individual crystal and is continued, as the glass becomes more viscous, by the growth of a spherulite about this crystal.

Silica, the fundamental constituent of nearly all glasses, is perhaps the commonest ingredient that separates from them. It may separate as minute crystals, evenly disseminated, when it gives an opalescent, milky or a dense opaque glass according to the size of the crystals. Under exceptional conditions large individual crystals of tridymite have been noted.[1] Finally it may

[1] H. Le Chatelier, *Bull. Soc. Min. Fr.*, **39**, 150 (1916).

separate in the form of spherulites which have special interest in this connection since they constitute typical stones.

The silica contained in spherulites of this type is, in the writer's experience, principally in the tridymite form though some cristobalite is usually present and occasionally may predominate. Though a spherulite may appear to be entirely crystalline it is really composed principally of glass with a relatively small proportion of crystals, the glass being interstitial between the radiating crystal fibres. While frequently of the same mineral constitution, these spherulites are unlike batch stones in that there is no central core of a dense crystalline nature free from glass, and there is, of course, never a core of quartz. The interstitial glass of tridymite spherulites is appreciably higher in refractive index than the main mass of glass surrounding the spherulite because there is an abstraction of silica from the interstitial glass. The glass surrounding a spherulite is, however, not appreciably affected by this action. A spherulite grows entirely, then, at the expense of the glass contained within it. It is for this reason that chemical analysis of a spherulite shows it to have sensibly the same composition as the main mass of glass, a fact which has sometimes led to the erroneous conclusion mentioned above, that the glass as a whole mass has crystallized.

The compound $CaSiO_3$ separates rather frequently from glass. This compound is known in two crystalline modifications, wollastonite, stable at temperatures below 1170° C, and pseudowollastonite, stable at higher temperatures. According to Le Chatelier, pseudowollastonite forms in some glasses,[1] but the writer has seen only wollastonite. In one example seen by the writer, fairly large individual crystals up to 3 mm. in length were found in plate glass. Usually, however, the wollastonite forms typical spherulites. Some spherulites of this type found in a window glass tank (see Fig. 2) and examined by the writer, show radiating prismatic fibres of wollastonite with some interstitial glass that is thickly dotted with minute crystals of cristobalite. Wollastonite crystals as found in glass have properties identical with those of the natural mineral and given on a later page.

Besides wollastonite, which may separate from ordinary lime-

[1] *Bull. Soc. Min. Fr.*, **39**, 150 (1916).

soda glasses, and silica, which may separate not only from these but also from many special glasses, there are certain compounds that separate only from special glasses.

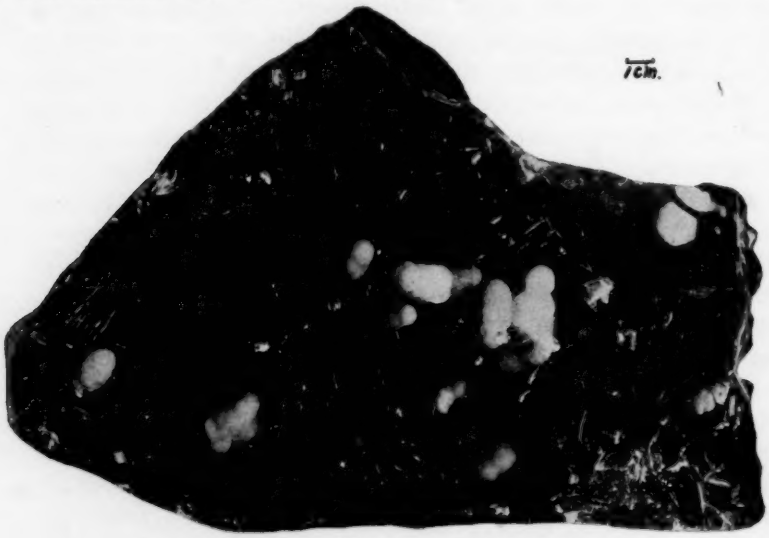

FIG. 2.—Spherulites of Wollastonite ($CaSiO_3$) in Glass.

From some barium crown glasses the compound $BaSi_2O_5$ may separate.[1] It may form fairly large individual crystals (see Fig. 3) if crystallization begins at a high temperature, and about these crystals spherulitic growth may take place as the temperature falls. If crystallization takes place entirely at the lower temperature a simple spherulite may form. Such spherulites or stones are readily distinguishable from other stones by the characteristic properties of $BaSi_2O_5$.

From glasses very rich in lead, spherulites sometimes separate, the fibres of which appear to agree in general properties with the natural mineral alamosite, $PbSiO_3$.

All spherulites have the same radiating fibrous structure that is described in connection with silica spherulites.

All of these types of devitrification stones are readily recognized

[1] N. L. Bowen, "Crystals of Barium Disilicate in Optical Glass," *J. Wash. Acad. Sci.*, **8**, 265 (1918).

as such by the characters that have been mentioned here in connection with them. The ability to recognize them may, in itself, be an important aid to the glass-maker, but the ability to determine the exact composition of the crystals that separate may be a still more important factor. The separation of a certain compound frequently indicates an excess of that compound in the glass and may point to mistakes made in the batch room or to variability in the composition of one of the raw materials. The nature of the compound separating suggests which one of the raw materials should be suspected. If these factors have

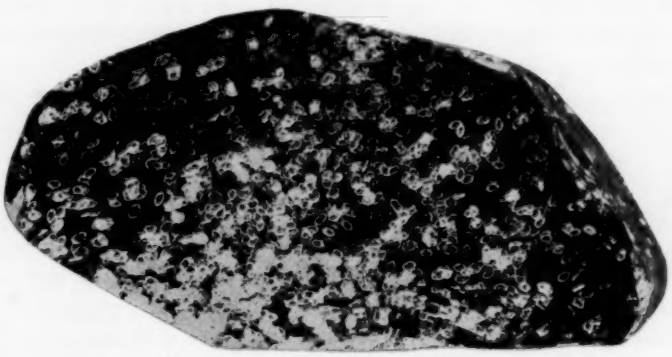

FIG. 3.—Crystals of $BaSi_2O_5$ in Glass. (Natural size).

been checked and found satisfactory, then the difficulty must be sought in an ill-chosen batch composition. Nearly always some readjustment in the chemical composition of a glass can be made without making a change of properties too great to spoil the glass for its particular use and the nature of the crystals that separate furnishes a clue to the direction in which this change of composition should be made. When a change of composition is not permissible, the glass-maker must endeavor to vary his heat treatment in such a way as to reduce the formation of the devitrification stones to a minimum.

Optical Properties of Crystals Occurring in Glass.

The following is not intended to be a complete statement of the optical properties of the crystals described. It gives merely those

properties that are of greatest use in distinguishing the crystals as they are found in the glass.

Sillimanite (Al_2SiO_5) is orthorhombic and occurs in glass in lath-shaped crystals with parallel extinction and positive elongation. The refractive indices are $\gamma = 1.681$ and $\alpha = 1.660$ and can be measured even on very small crystals embedded in glass, for by careful search of the powder immersed in liquid one can always find crystals that have not been broken across and therefore present an edge against the liquid. The refraction is higher than that of all glasses except the very heavy lead glasses, which fact enables one to distinguish even excessively minute crystals from those of cristobalite or tridymite. The double refraction, $\gamma - \alpha = 0.021$, is moderately strong.

Silica may occur in glass in any of the three forms *quartz*, *tridymite* or *cristobalite*.

Quartz occurs only rarely and then as sand that has remained unaltered. It is uniaxial and positive; $\epsilon = 1.553$ and $\omega = 1.544$.

Tridymite occurs as thin hexagonoid plates that appear as needles when turned on edge and have parallel extinction and negative elongation. They frequently show the characteristic parallel growth of overlapping plates. The refractive indices are 1.469 – 1.473, the refraction and double refraction being therefore both very low.

Cristobalite frequently occurs as skeleton crystals consisting of minute octahedra arranged in parallel growth on a cubic pattern and having a general similarity to magnetite, native gold or other cubic minerals when they form skeleton crystals. When free to grow larger it may form elongated cubes that are, however, never sufficiently elongated to be confused with "needles" of tridymite. The cubes are sometimes terminated by octahedra that have somewhat greater dimensions than the cube and give club-shaped or spear-shaped crystals. The refractive indices are 1.484 – 1.487, somewhat higher than those of tridymite. Probably as a result of the compensating effect of intricate twinning, cristobalite usually appears to be nearly isotropic.

Barium disilicate ($BaSi_2O_5$), is orthorhombic and occurs as thin six-sided plates (see Fig. 3) with parallel extinction and negative

elongation. The refractive indices are $\gamma = 1.617$ and $\alpha = 1.598$.[1] In connection with the sign of the elongation it should be noted that a lath-shaped section representing a plate broken across may be either positive or negative.

Wollastonite ($CaSiO_3$), though monoclinic, appears in glass as crystalline needles or laths with parallel extinction, because elongated parallel to *b*, the axis of symmetry. The elongation is either positive or negative, depending on the plane in which the lath is turned. The refractive indices are $\gamma = 1.633$ and $\alpha = 1.620$.

Summary.

The petrographic microscope is a convenient and efficient instrument for the determination of the nature and origin of "stones" or crystalline particles occurring in glass. Stones are divided into four classes: (1) *pot stones*, (2) *batch stones*, (3) *crown drops*, (4) *devitrification stones*. These classes have distinctive features of structure and texture that are revealed by the microscope. Moreover, the crystalline phases contained in stones can be identified by a determination of their optical properties. The results of a study of stones by these methods are given in this paper.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., December, 1918.

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[1] For a more complete description of barium disilicate see N. L. Bowen, *J. Wash. Acad. Sci.*, **8**, 265 (1918).

SOME TYPES OF PORCELAIN.[1]

By F. H Riddle and W. W. McDanel, Pittsburgh, Pa.

Introduction.

The present work deals with porcelain bodies burned at temperatures equivalent to the softening point of cone 10 or above. This includes the firing range of electrical porcelain and of most hotel china as well as of wares fired to higher temperatures—such as chemical porcelain and some of the imported chinas. Some table porcelain made in the United States is burned to cone 13 or 14 but the production is very small. Some of the French, Austrian and other imported wares are burned at from cone 15 to 18.

The European practice is to bisque the ware at a low temperature and to carry the glost temperature to the maturing point of the body. This, of course, necessitates the use of a glaze maturing at the same temperature as the body. The glaze and body are thus brought into very intimate contact, since the glaze, as it softens, is absorbed by the porous body before the latter closes up and becomes impervious. This penetration of the glaze is merely along the surface but is sufficient to produce a strong bond between the body and glaze.

The American practice is to mature the body in the bisque burn and to use a glaze which matures at a lower temperature. For example, we may bisque to cone 11 and glaze to cone 4 or 5. This method has many manufacturing advantages. It is not, however, the purpose of this paper to discuss the relative merits of the two processes.

The Field Covered.

The chief purpose of this study was to determine the burning range of porcelain bodies having compositions covering the ordinary porcelain field fired at cone 10 and above. In Table 1 are given the compositions of the bodies used. It will be noted that the clay content varies from 45 to 85 per cent and that the

[1] By permission of the Director, Bureau of Standards.

TABLE 1.[1]

COMPOSITIONS USED.

Body number.	Clay content. Per cent.	Feldspar content. Per cent.	Whiting content. Per cent.	Flint content. Per cent.
16 to 23	45	16–30	...	39–25
24 to 31	50	16–30	...	34–20
32 to 39	55	14.5–28.5	1.5	29–15
40 to 47	60	14.5–28.5	1.5	24–10
51 to 55	70	10–28.5	1.5	18.5–0
56 to 59	75	10–23.5	1.5	13.5–0
60 to 62	80	10–18.5	1.5	8.5–9
63	85	13.5	1.5	0

flux content varies from 10 to 30 per cent. In several of the bodies of high clay content the flux content has necessarily been

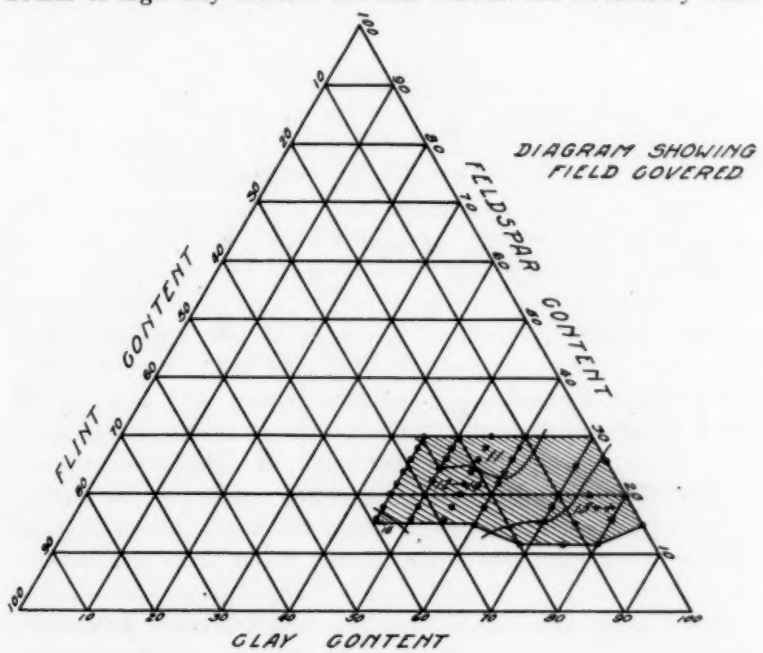

FIG. 1.

[1] The clay content was made up of equal parts of Georgia, Florida, North Carolina and Delaware kaolins. Where the clay content was over 55 per cent the balance was calcined to cone 14 and ground dry to pass a 120 mesh sieve.

reduced. No ball clay was used in any of the bodies of the first series, the clay content having been derived from equal parts of four American clays, namely, North Carolina, Florida, Georgia and Delaware kaolins. In all cases in which the clay content was more than 55 per cent, the balance was calcined. It would not, of course, be a common practice in the manufacture of ware, excepting in a few cases, to entirely eliminate ball clay. The effect of ball clay is shown later. It is a fact that most of the vitreous pottery bodies made in this country at the present time contain but small amounts of ball clay. In the triaxial diagram (Fig. 1) is shown the field covered.

Methods of Testing.

The method of procedure in testing the different bodies was that ordinarily used in work of this kind. The bodies were weighed out from standard grade materials—previously dried so that no allowance was necessary for moisture. Two five-kilogram charges of each body were weighed out and ground wet for three hours in a ten-inch ball mill. Throughout the work all conditions of testing were maintained as nearly constant as possible. After grinding, the two bodies were mixed, passed through a 140-mesh silk lawn, and filter-pressed. The filter cakes were then thoroughly hand-wedged and made into ware. Unless otherwise noted, the material was made up into ware three days after having been filter-pressed. The only bodies that were prepared under different conditions were those made with varying times of grinding and with varying times of ageing. The bodies were molded principally into draw trial pieces and standard cups for the determination of the dielectric resistance. In certain cases moduli of rupture bars, crushing cubes, and pieces of chemical- and table-ware were made, this depending upon the character of the body.

The tests on each body included the determination of the water of plasticity, the drying shrinkage (by volume), the apparent specific gravity in the dried state, and the porosity and volume changes at different firing temperatures. In some cases additional tests such as the transverse, crushing, etc., were made.

Water of Plasticity.

The previously prepared clay, in the proper working condition, was forced from a hydraulic-plunger press through a die $1^1/_8''$ square (with slightly rounded corners). The bars were cut into test pieces $1^1/_2$ inches long. For the determination of the water of plasticity, three of the pieces were weighed immediately after being made and again after having been thoroughly dried at 110° C.

Drying Shrinkage.

In making this determination the wet briquettes were immersed in kerosene immediately after molding and weighing. The volumes were then determined in a voluminometer of the Seger type, provided with a burette reading to 0.05 cc. After removing the specimens, they were dried, first at atmospheric temperatures and finally at 110° C. The dry specimens were weighed at once, again immersed in kerosene (usually for twelve hours) and the volumes were then determined as before. The shrinkage was computed in terms of the dry volume. From the weights of the dry specimens and their volumes, the apparent specific gravities were computed.

From the wet and dry weights and the wet and dry volumes of the briquettes and the true specific gravity of the clay, it was possible to calculate the volume of the shrinkage and the pore water in terms of the true clay volume. These computations were based on the following relations:

$$\frac{100\,S\,(W_1 - W_2) = a}{W_2} = \left\{ \begin{array}{l} \text{volume of shrinkage water, in terms of the true clay substance, expressed in per cent.} \end{array} \right.$$

$$\frac{100\,S\,(V_1 - V_2) = b}{V_2} = \left\{ \begin{array}{l} \text{volume of shrinkage water, in terms of the true clay substance, expressed in per cent.} \end{array} \right.$$

In these formulas:

S = Specific gravity of body (approaching the value of 2.6 quite closely)

W_1 = weight of briquette in the wet state

W_2 = weight of briquette in the dry state

V_1 = volume of briquette in the wet state

V_2 = volume of briquette in the dry state

The value $a - b$ represents, similarly, the volume of pore water and the ratio $\frac{a-b}{a}$, the relation of pore to shrinkage water. By dividing b by a, and multiplying by 100, the percentage of shrinkage in terms of the volume of total water may be computed.

Modulus of Rupture.

Test pieces in the form of bars $7'' \times 1'' \times 1''$ were carefully molded from a thoroughly wedged piece of clay by wire cutting to as near the mold size as possible and then carefully placing in the mold in one piece, pressing in, and trimming off with a wire at the top. The properly numbered pieces were dried at room temperature, heated at 110° C, cooled in a desiccator, and immediately broken transversely. In all cases ten pieces were broken and the average result taken.

Burning Behavior of the Clays.

The draw trial briquettes, after having had their dry volumes determined, were placed in a test kiln, fired with natural gas and compressed air, and burned at a rate corresponding to a temperature increase of 20° C per hour above 800° C. Beginning at 1200° C, the briquettes were drawn from the kiln at intervals of 30° C. This was continued up to 1440° C and, in case the bodies were extremely refractory, the temperatures were carried higher until the pieces became overburned. All pieces, as they were drawn from the muffle, were placed as rapidly as possible in an annealing furnace and cooled down gradually in order to prevent shattering. When cool, the briquettes were weighed, immersed in water, boiled in a partial vacuum for five hours, again weighed suspended in water, and finally weighed in air when fully saturated with water.

From these data, the porosity was calculated by the use of the Purdy formula.[1] The volumes of the briquettes were determined by means of the voluminometer—kerosene being used as the displacing liquid. The volume shrinkage or expansion was invariably expressed in terms of the original volume in the dried state. Both the porosity-temperature and the volume-temperature rela-

[1] R. C. Purdy, Ill. Geol. Surv., *Bull.* 9.

tions are extremely significant in the study of the burning range and behavior of a body. When plotted, the information presents an easy method of study and comparison. Zero porosity, or better, zero absorption, may be considered the first point of maturity. A more sensitive criterion of maturity is the point of greatest density or smallest volume and it should correspond to the most suitable temperature for burning the ware. As soon as overburning—due to the formation of a vesicular structure—starts, the volume increases and a drop in the curve is noted. It is evident, then, that the greater the difference in temperature between the point at which zero porosity is first reached and that at which overburning is evident, the wider is the firing range of a body. When the overburning advances far enough, there will be an increase in porosity—due to water entering some of the outside pores that have been ruptured. The volume change will, therefore, indicate overfiring earlier than the porosity relation.

Considerable care and accuracy is necessary in making draw trial burns in order to make comparison possible between several burns. Thus far, seven burns have been made in the work under discussion. The kiln was large enough to hold all of the briquettes for seventeen bodies. As a check against the thermo-couple and pyrometric cones, it has been our practice to burn a set of draw trials of the same body in several burns and to check the results by comparison.

The Effect of Increasing the Feldspar Content and Maintaining the Clay Content Constant.

This is very well illustrated in Fig. 2. The bodies used were Numbers 17, 19, 21 and 23 of Table 1, their compositions together with their burning ranges being given in Table 2.

TABLE 2.

	Composition.					
No.	Per cent clay content.	Per cent feldspar content.	Per cent flint content.	Temp. of zero absorption.	Temp. of maximum density.	Temp. of start of overburning.
17	45	18	37	1380° C	1410° C	1440° C+
19	45	22	33	1350° C	1380° C	1410° C+
21	45	26	29	1320° C	1350° C	1410° C—
23	45	30	25	1320° C	1350° C	1380° C

A study of the results shows that the range is not much wider for the low feldspar than for the high feldspar bodies—though there is some difference. This is better shown by the curves than by the numerical values. The curves also indicate

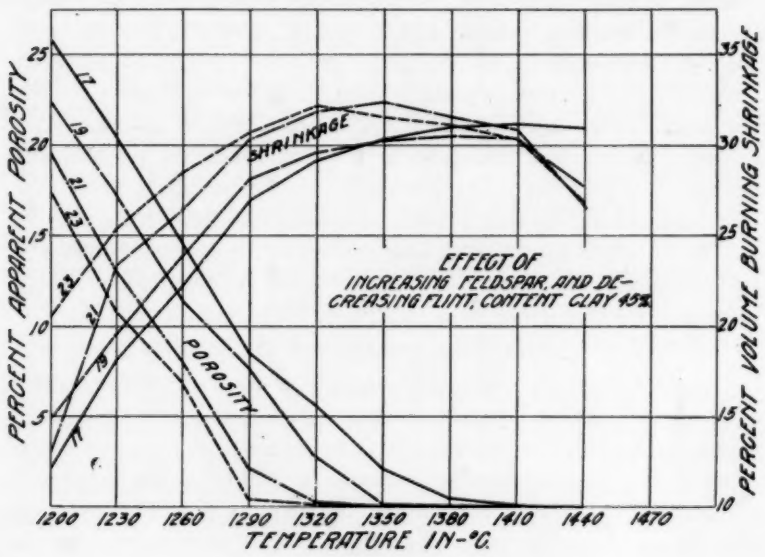
PERCENT APPARENT POROSITY
PERCENT VOLUME BURNING SHRINKAGE
SHRINKAGE
POROSITY
EFFECT OF INCREASING FELDSPAR AND DECREASING FLINT, CONTENT CLAY 45%
TEMPERATURE IN °C.
1200 1230 1260 1290 1320 1350 1380 1410 1440 1470
25 20 15 10 5
35 30 25 20 15 10

FIG. 2.

that the bodies of high feldspar content appear to approach zero absorption more abruptly. Although the firing ranges of the several bodies are nearly the same, the temperatures of maturity are much lower in the case of the high feldspar bodies—as would naturally be expected.

This same type of curve applies to bodies having a much higher content of clay—up to 75 per cent. In Fig. 3 it will be noted that bodies Nos. 52 and 55 contain 70 per cent clay and that body No. 52 contains $16^1/_2$ per cent flux and body No. 55 contains 30 per cent flux.

The chief difference in the two sets of bodies, as shown by Figs. 2 and 3, is that the variation in the content of flux has a more marked effect on the low clay (Fig. 2) than on the high clay bodies (Fig. 3). This would indicate, therefore, that the higher

the clay content, the less the effect of variations in the amount of flux. The difference, however, is not great. In fact, it is rather surprising how little difference there is in the burning

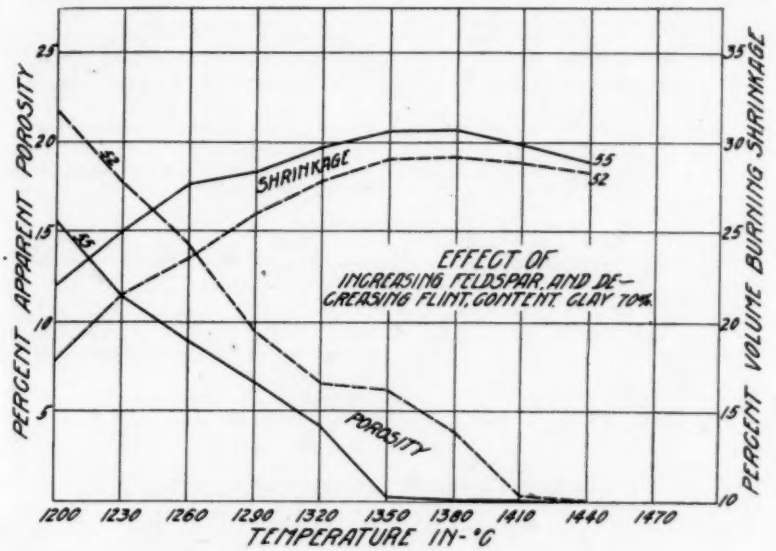

FIG. 3.

ranges of bodies having varying clay contents, so long as the amount of flux used is constant, the flint content decreasing, of course, as the clay content increases.

In Fig. 4 is shown the burning curves for the three bodies, the compositions of which are given in Table 3.

TABLE 3.

Body No.	Per cent raw clay.	Per cent calcined clay.	Per cent feldspar.	Per cent whiting.	Per cent flint.
35	55	..	20.5	1.5	23.0
43	55	5	20.5	1.5	18.0
53	50	20	19.0	1.5	9.5

As noted, these bodies contain 55 per cent, 60 per cent and 70 per cent of clay, respectively. The burning curves for Nos. 35 and 43 are very much alike. Body No. 53 contains less fluxing

material and hence has a somewhat smaller shrinkage but otherwise it is similar to the others.

Referring again to Fig. 2, the burning curves for body No. 19, containing 45 per cent clay and 22 per cent feldspar, is also similar to that of these bodies.

It is interesting to note the similarity in the curves for the bodies represented in Fig. 4, which have variations in clay content

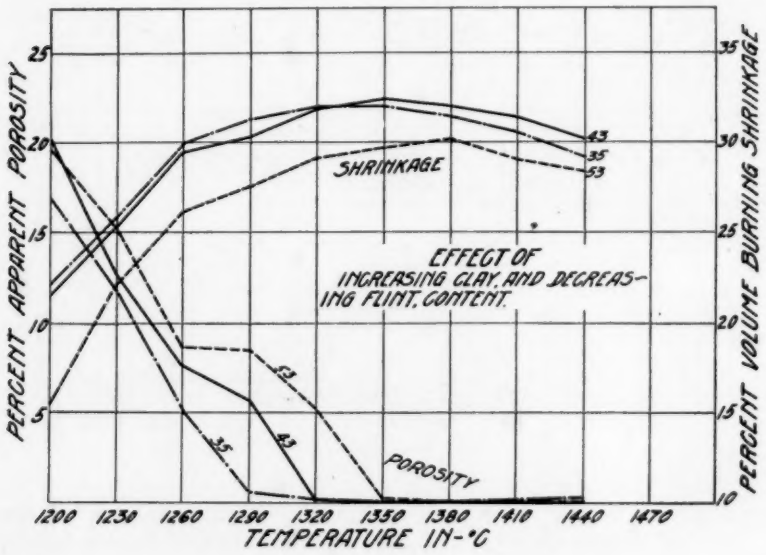

FIG. 4.

from 55 to 70 per cent but the same content of flux, to the bodies shown in Fig 2, which have the same clay content but a wide variation in the flux content. Although body No. 53 does not have exactly the same content of flux as Nos. 35 and 43, it is sufficiently close for comparison and it will be noted that it is a little more refractory than bodies Nos. 35 and 43.

Fig. 5 is an enlarged sketch of the field covered, as shown in Fig. 1, and shows the maturing points of the bodies in the different areas.

It will be noted that the bodies containing 45 and 50 per cent clay vitrify at a slightly higher temperature than those contain-

ing 55 and 60 per cent clay. This, however, is due to the presence of $1^1/_2$ per cent whiting in the bodies containing 55 per cent and more of clay. The effect of the whiting is shown later.

In this connection, it is of interest to note the softening points of mixtures of Zettlitz kaolin, quartz and feldspar as determined

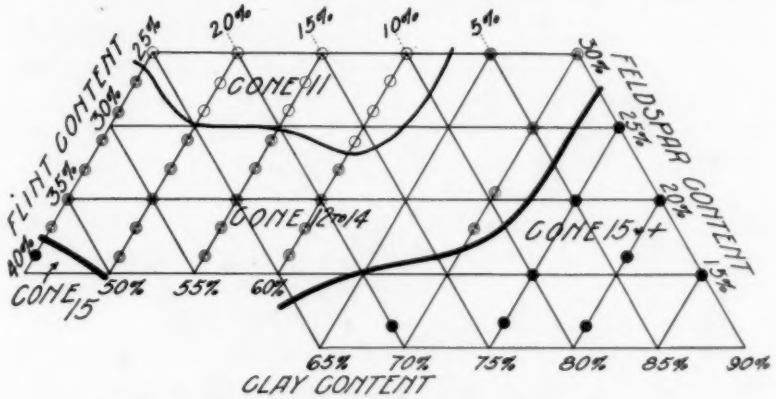

DIAGRAM SHOWING MATURING POINTS OF DIFFERENT MIXTURES.

FIG. 5.

by M. Simonis.[1] These have been plotted on the triaxial diagram, Fig. 6. The field covered in Fig. 5 is shown in the shaded area of Fig. 6. There is very little variation in the softening points between 45 and 70 per cent kaolin with feldspar variations from $12^1/_2$ to 30 per cent. There is also more variation between $12^1/_2$ per cent and 30 per cent feldspar with 45 per cent clay than with 70 per cent clay.

The Effect of Ball Clay.

As previously stated, ball clay was not used in any of the bodies prepared in the foregoing work. On account of its general use and its bonding strength in the green state, tests were made in order to show its effect both in the green state and in the burning. In Table 4 is shown the composition of several bodies, their moduli of rupture, water of plasticity contents, etc. The first four

[1] *Sprechsaal*, 1907, No. 40.

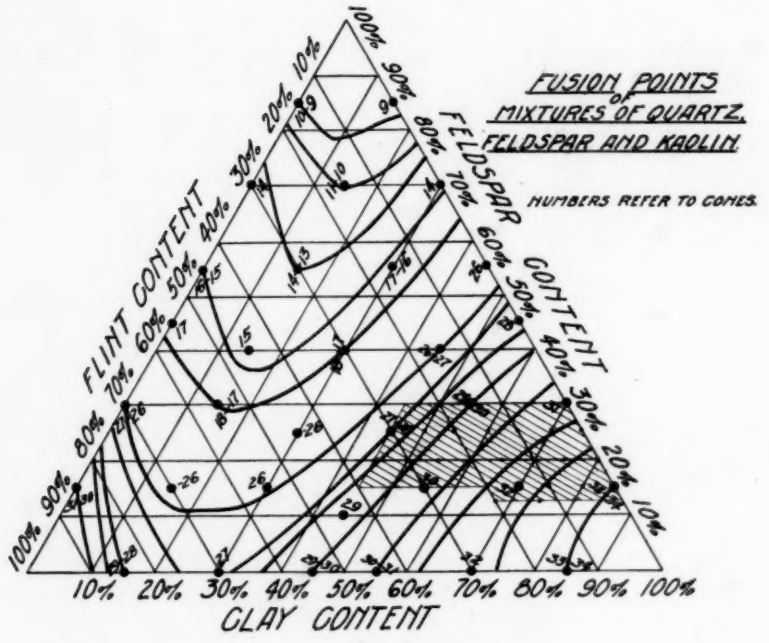

FIG. 6.

are all-kaolin bodies and the remainder of the series contain from 0 to 16 per cent of Tennessee ball clay. Of the first four, two

TABLE 4.

Showing the effect of ageing of bodies containing no ball clay as compared to green bodies containing ball clay.

Body No.	Time aged.	Drying (shrinkage by volume).	Per cent water in terms of dry wt.	Modulus of rupture, lbs. per sq. in.	Per cent ball clay.	Per cent total clay.	Per cent feldspar.
26 old	8 months	19.54	28.12	267.6	0	50	20.0
26 new	3 days	13.98	27.80	139.8	0	50	20.0
34 old[1]	8 months	22.67	31.23	278.8	0	55	18.5
34 new[1]	3 days	14.75	28.70	165.0	0	55	18.5
139 new	3 days	10.25	25.81	157.0	0	45	20.0
140	3 days	11.99	26.44	186.0	4.0	45	20.0
141	3 days	12.07	25.92	201.5	8.0	45	20.0
142	3 days	13.60	26.24	202.0	12.0	45	20.0
143	3 days	14.02	26.32	250.0	16.0	45	20.0

[1] Bodies Nos. 34, old and new, contain 1½ per cent of whiting.

were molded into test pieces three days after preparation and duplicates of these were also molded into test pieces after ageing for eight months—having been kept in a damp closet and in workable condition for the entire time. None of the other bodies were aged.

In both cases when the body was aged the all-kaolin bodies showed a marked increase in strength with age. Ageing increased the modulus of rupture of body No. 26 from 139.8 pounds to 267.6 pounds per sq. in. and of body No. 34 from 165 to 278.8 pounds per square inch. In both cases the aged kaolin bodies were stronger than body No. 143, containing 16 per cent ball clay, the modulus of rupture of this body being 250 pounds per sq. in. It may be of interest to compare the strength of these bodies with the strength of commercial bodies. Several commercial china bodies were tested and their moduli of rupture were found to vary from 170 pounds to 220 pounds per square inch. Several attempts were made to model difficult shapes from the un-aged kaolin bodies. Comparing this with the modeling with the aged kaolin bodies the difference was remarkable.

This is not a proof that ageing will improve the working properties of all bodies, but in view of the fact that it is desirable to make ware as white as possible, it is well to reduce the ball clay content of bodies to as low a figure as possible. If ageing will make this possible it is well worth doing. Several potters, who grind their pottery bodies exceedingly fine, claim that they become unworkable if aged and that the clay at the bottoms of the piles becomes "rubbery," as does clay that contains an excess of alkaline salts. This is quite possible as the fine grinding may reduce the particles of feldspar to such an extent that a part of the salts will become soluble in time and act as casting salts do. If this is true, it then becomes a case of sacrificing one quality for the other and of depending entirely upon what the potter considers the best thing to do. On the other hand, it may be possible to neutralize the alkaline salts by the addition of acid before grinding.

The effects of increasing the ball clay content and the length of time of ageing of bodies are well marked in the burning. In Fig. 7 is shown the volume shrinkage and porosity curves for bodies Nos. 139 to 143, inclusive. The curves show the very

marked effect the ball clay has on the tendency of the body to overburn as well as how increase of ball clay tends to close the body up at lower temperatures—as shown by the porosity curves. Bearing in mind that body No. 139 has about the same composition as body No. 17, it might be well to compare the curves of Figs. 2 and 7. The two sets of curves have quite different characteristics. In Fig. 2 is shown the effect of increasing amounts of feldspar. The increase not only causes the body to overburn at

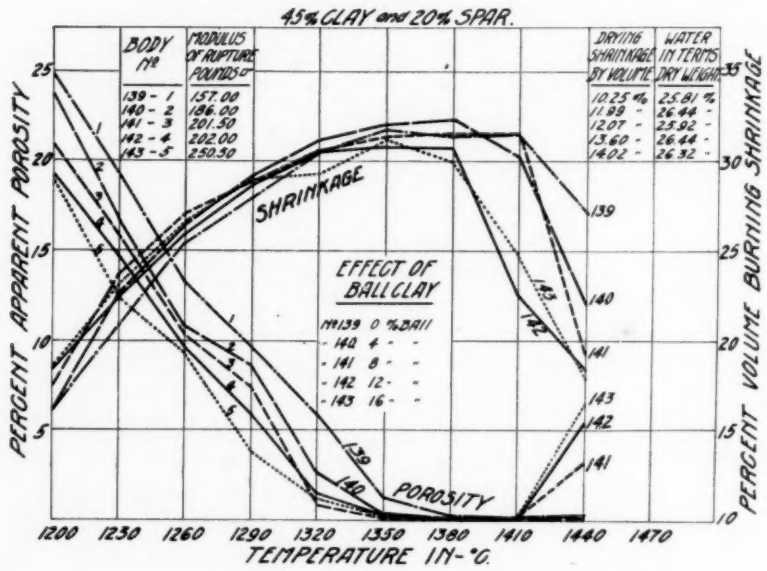
45% CLAY and 20% SPAR.
BODY No
MODULUS OF RUPTURE POUNDS
DRYING SHRINKAGE BY VOLUME
WATER IN TERMS DRY WEIGHT
139 - 1 157.00 10.25 % 25.81 %
140 - 2 186.00 11.99 - 26.44 -
141 - 3 201.50 12.07 - 25.92 -
142 - 4 202.00 13.60 - 26.44 -
143 - 5 250.50 14.02 - 26.32 -
SHRINKAGE
EFFECT OF BALL CLAY
No 139 0 % BALL
- 140 4 - -
- 141 8 - -
- 142 12 - -
- 143 16 - -
POROSITY
PERCENT APPARENT POROSITY
PERCENT VOLUME BURNING SHRINKAGE
TEMPERATURE IN - °C.
1200 1230 1260 1290 1320 1350 1380 1410 1440 1470
25 20 15 10 5
35 30 25 20 15 10

FIG. 7.

a lower temperature but causes it to mature at a lower temperature—the firing range remaining about the same. However, the addition of ball clay, although it matures the body at a lower temperature (compare porosity curves, Fig. 7), also causes it to overburn much earlier in proportion. Up to a certain point, the addition of ball clay will permit of the reduction of the feldspar content.

When these results are compared with those shown in Figs. 8 and 9, the effect of ageing upon the burning behavior of bodies

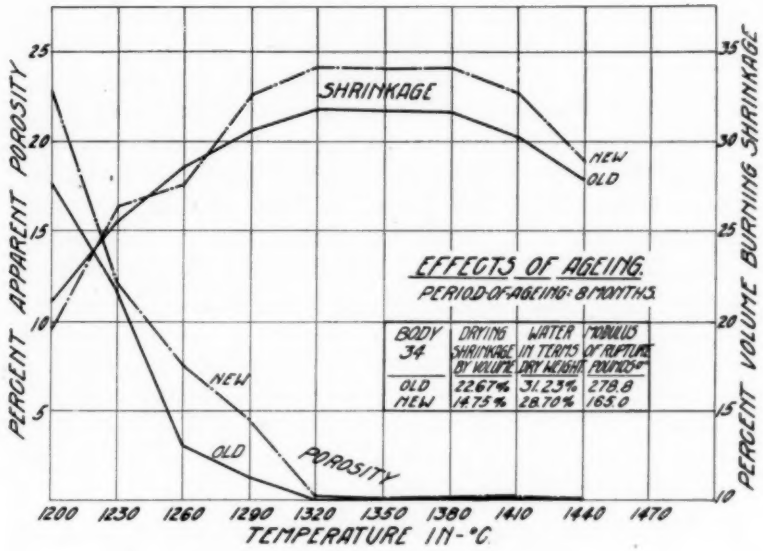
PERCENT APPARENT POROSITY
PERCENT VOLUME BURNING SHRINKAGE
SHRINKAGE
NEW
OLD
POROSITY
EFFECTS OF AGEING.
PERIOD OF AGEING: 8 MONTHS.
BODY 34 | DRYING SHRINKAGE BY VOLUME | WATER IN TERMS OF DRY WEIGHT | MODULUS OF RUPTURE POUNDS
OLD | 22.67% | 31.23% | 278.8
NEW | 14.75% | 28.70% | 165.0
1200 1230 1260 1290 1320 1350 1380 1410 1440 1470
TEMPERATURE IN °C.

FIG. 8.

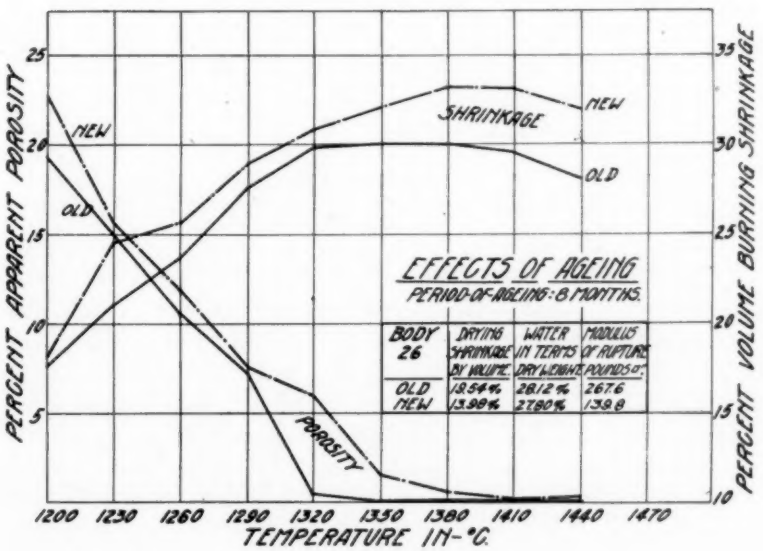
PERCENT APPARENT POROSITY
PERCENT VOLUME BURNING SHRINKAGE
SHRINKAGE
NEW
OLD
POROSITY
EFFECTS OF AGEING
PERIOD OF AGEING: 8 MONTHS.
BODY 26 | DRYING SHRINKAGE BY VOLUME | WATER IN TERMS OF DRY WEIGHT | MODULUS OF RUPTURE POUNDS
OLD | 18.54% | 28.12% | 267.6
NEW | 13.90% | 27.80% | 139.8
1200 1230 1260 1290 1320 1350 1380 1410 1440 1470
TEMPERATURE IN °C.

FIG. 9.

Nos. 26 and 34 is apparent. The aged bodies close up somewhat earlier and their shrinkage is less. The curves would also indicate that the ware burns much more uniformly. It has been seen that the difference in the transverse strength of the fresh and aged bodies is greater than that of the body containing zero and that containing 16 per cent ball clay. At the same time the burning range of the fresh and aged bodies is, if anything, in favor of the aged or tough body. On the other hand, in the case of ball clay bodies, the increase of ball clay has a marked effect in the shortening of the firing range. This, then, is still another point in favor of the use of bodies having a minimum content of ball clay but which are improved by ageing. All of the above observations, especially that the aged bodies shrink less than the fresh ones, show that the ageing has a profound influence upon the colloidal portion of the body. If ball clay must be used, as little as possible should be employed.

The Effect of the Addition of Small Amounts of Magnesium, Calcium and Barium Carbonates.

Four sets of bodies were made up with the following body as a base:

6 per cent ball clay
39 per cent kaolin
18 per cent feldspar
37 per cent flint

This body was selected as it contains about as little ball clay as is ordinarily used commercially and a fairly low content of feldspar. Small amounts of flux were introduced for the purpose of securing bodies having lower maturing temperatures. In each case the feldspar was replaced by equal amounts of another flux. The amounts added are given in Table 5.

TABLE 5.

Series 1.		Series 2.		Series 3.		Series 4.	
Body No.	Per cent flux.	Body No.	Per cent flux.	Body No.	Per cent flux.	Body No.	Per cent flux.
164	0.2 MgO	168	0.2 CaO	172	0.2 MgOCaO	176	0.2 BaO
165	0.4 "	169	0.4 "	173	0.4 "	177	0.4 "
166	0.7 "	170	0.7 "	174	0.7 "	178	0.7 "
167	1.0 "	171	1.0 "	175	1.0 "	179	1.0 "

The alkaline earths were introduced as the carbonates. In the third series, equal equivalents of CaO and MgO were added as carbonates.

The curves of Figs. 10, 11 and 12 show very well the effect of the fluxes upon the burning range. The curves for bodies Nos. 172 to 175 are not shown as they are similar to those of bodies Nos. 164 to 167. The principal points to be noted are that BaO shows no noticeable action other than a slight tightening of the body while CaO and MgO produce a very decided effect,

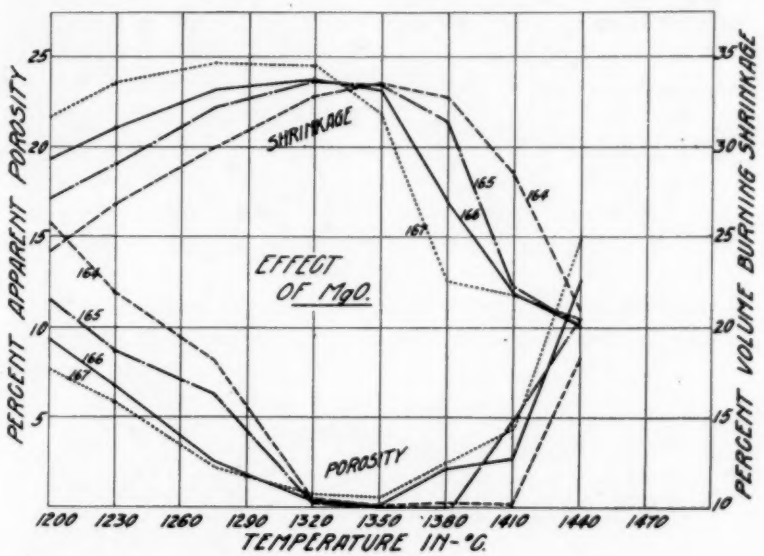

FIG. 10.

the MgO, however, being the more active. It is also very noticeable that the CaO does not hasten the maturing of the body but causes overburning at a lower temperature. Its presence also shortens the firing range considerably. On the other hand, MgO causes the body to mature much earlier and brings about the overfired state at a lower temperature—the former effect being the more prominent. The mixture of the two oxides behaves almost exactly like MgO by itself.

These facts would point to the conclusion that the addition of

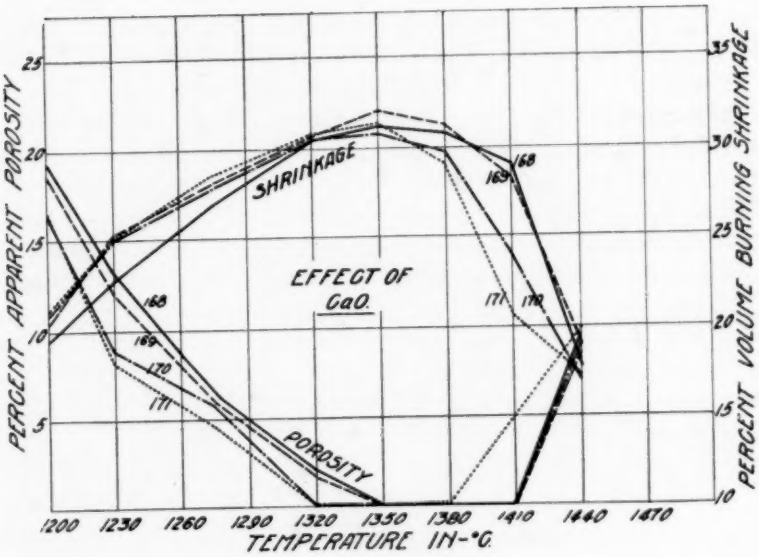
PERCENT APPARENT POROSITY
PERCENT VOLUME BURNING SHRINKAGE
SHRINKAGE
POROSITY
EFFECT OF
CaO.
168
169
170
171
TEMPERATURE IN-°C.
1200 1230 1260 1290 1320 1350 1380 1410 1440 1470

FIG. 11.

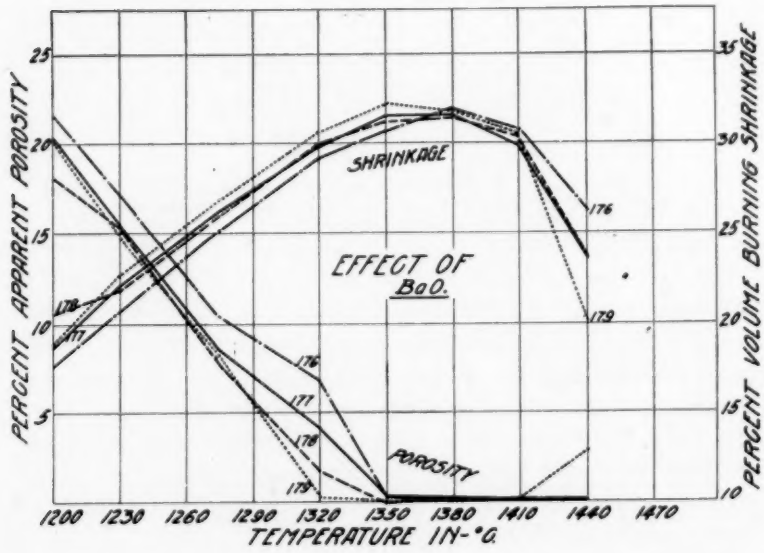
PERCENT APPARENT POROSITY
PERCENT VOLUME BURNING SHRINKAGE
SHRINKAGE
POROSITY
EFFECT OF
BaO.
176
177
178
179
TEMPERATURE IN-°C.
1200 1230 1260 1290 1320 1350 1380 1410 1440 1470

FIG. 12.

a small quantity of magnesite or dolomite would be very beneficial but that the addition of whiting would tend to hasten overburning even though it would assist vitrification of the body. BaO seems to render no useful service. It is also noted that volume shrinkage is greater with the addition of the MgO and MgOCaO than with the addition of CaO or BaO. Those bodies from No. 164 to 179 were made up into ware by several methods.

The body containing no flux, beyond the 18 per cent feldspar, showed no translucency when fired at cone 11, while the bodies to which were added the alkaline earths (with the exception of the barium carbonate) evidenced very marked translucency increasing with the amount added, although there was not a great difference between the effects of the 0.7 per cent and 1.0 per cent additions. The BaO produces no translucency. With increase in translucency there was noted a marked change in color from yellowish to bluish white, particularly in ware that was burned under reducing conditions, although this was also observed in the ware fired under oxidizing conditions.

The addition of small amounts of magnesite or dolomite is beneficial in many ways, particularly to those bodies which should mature at from cone 10 to 11.

Special Bodies.

In view of the fact that hard-fire porcelain bodies develop more or less well-defined crystalline sillimanite, it was decided to replace all of the quartz in some bodies by artificial sillimanite—a mineral having a low coefficient of expansion and not subject to crystalline transformations as is the quartz. The sillimanite calcine was prepared in several ways but the most satisfactory procedure was to calcine a thoroughly blended mixture of 258 parts of kaolin and 102 parts of anhydrous alumina. These constituents were ground dry in a ball mill with 2 per cent by weight of powdered boric acid, mixed with water, pugged into a stiff mass, and then molded into small lumps about an inch or two in diameter. These were calcined to cone 20. The boric acid accelerated the reaction and apparently did no harm—probably volatilizing at a fairly low temperature. The calcined material was ground dry to pass a 100 mesh sieve and was then introduced into the body in the same manner as the other materials.

A petrographic examination of the calcine showed the presence of about 10 per cent of large sillimanite crystals (0.01 to 0.03 mm. long), 40 to 50 per cent of the ground mass being weakly bi-refringing and probably composed of very minute sillimanite crystals too small for accurate measurement. There were also traces of what appeared to be a minute amount of uncombined Al_2O_3.

A body having the following composition was prepared:

BODY NO. 50.

Sillimanite calcine	22.5 per cent
Kaolin	51.0 per cent
Feldspar	25.0 per cent
Whiting	1.5 per cent
	100.0

The burning range is shown by the curve in Fig. 13 and requires no explanation. Its long temperature range should be noted. The sillimanite having been introduced in the place of flint, the body is free from the strains due to volume changes caused by the

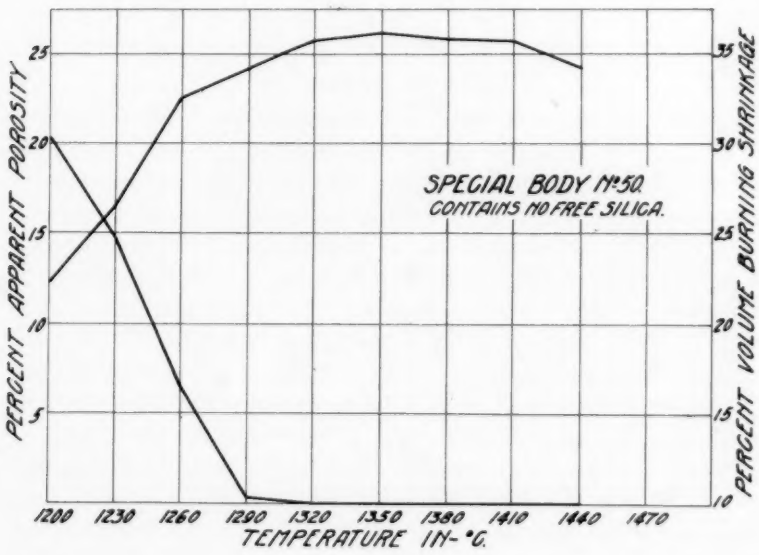

FIG. 13.

transformation of quartz. Sillimanite has proven useful in the preparation of bodies of different compositions—particularly where a low coefficient of expansion is desired. It is to be hoped that natural deposits of this mineral will be found in quantity. It has also been found that the sillimanite calcine may be incorporated with the flux used in the body—which makes it possible to reduce the calcination temperature to as low as the softening temperature of cone 14. A natural deposit, however, would be ideal for use providing the content of iron oxide were sufficiently low.

Cone 11 Bodies.

A number of the bodies in the field covered are within the range of commercial bodies fired from cones 10 to 12, even though the clay content be as high as 60 per cent. All things considered, the range of body composition for ware fired to from cones 10 to 12 (such as hotel china) would lie between the following limits:

Flint	30	to	40	per cent
Feldspar	14	to	18	per cent
Alkaline earth fluxes	4.0	to	0.5	per cent
Ball clay	3	to	8	per cent
China clay	45	to	25	per cent
Florida clay	10	to	6	per cent

It is evident, of course, that it would not be permissible to use a high feldspar content together with a high alkaline earth content. Dolomite is found in nature sufficiently pure for use in pottery bodies and can be secured at a very low cost. The lime, magnesia, or dolomite fluxes are of considerable aid in securing a whiter color.

Florida kaolin may be used to a certain extent as a substitute for ball clay, but should not be depended upon entirely in the manufacture of thin or medium-weight ware.

The limits given for ball clay are lower than some potters are probably using but they are as high as is necessary under working conditions where reasonable care is used. This statement is made after careful consideration and actual knowledge of the working qualities of such bodies.

Color.

In many wares, and particularly in table wares, color is one of the most important factors connected with their sale and must receive serious consideration. Sometimes other qualities must be sacrificed in order that the color may be as nearly white as possible. This is to be regretted but must be contended with as long as the trade demands it. Some of the most beautiful ware made in America is cream colored and is finding a large market. There is nothing more pleasing than cream-colored ware and it is a mystery as to just why china should be white.

There are three ways of securing white porcelain: first, the use of very pure materials; second, burning under reducing conditions; and third, masking the yellow color with a blue stain. The first method is ideal but practically out of the question. However, the purity of all materials must be considered and the quality maintained at as high a standard as the grade of ware will warrant.

As previously stated, the addition of small amounts of alkaline earth fluxes, such as dolomite, magnesite or whiting, improves the color regardless of any other treatment the body may receive.

The second method is largely used in Europe and when properly carried out results in a purer white than is produced by a stain. The ferric oxide is reduced to the lower oxides which, owing to their dark color and fineness of grain, produce a whiter effect. Care must be taken to start the reduction at a sufficiently low temperature so that the reducing gases may penetrate the structure completely and thus bring about the desired effect. The bisque burn is carried to a low temperature and the glost burn brought to maturity in the following way: The burn is divided into three parts, *viz.*, the heating-up period, the reducing period, and the finishing period. Oxidizing conditions are maintained during the heating-up period—which extends from the beginning of the burn to the softening point of cone 09.

The reducing period extends from cone 09 to cone 8—the latter point depending somewhat upon the constitution of the body and of the glaze. During the reducing period, carbon monoxide and hydrogen should be present in the kiln gases in quantities from 3 to 5 per cent. Too heavy reduction should be avoided. If

reduction is too strong when the glaze begins to soften and the body begins to tighten up, the ware may be spoiled by the deposition of carbon in the body or softened glaze.[1]

The third procedure, the use of cobalt stain, represents the familiar effect of the bluing used in washing clothes. It is evident that the use of one color in order to mask another cannot be as satisfactory, as far as quality of shade is concerned, as the total elimination of the yellow color. However, for ordinary purposes, the difficulty of securing proper reduction warrants the use of a stain. The cobalt is preferably introduced as the precipitated basic carbonate (obtained by the addition of sodium carbonate to a solution of cobalt salt), followed by one or two washings by decantation. The precipitated carbonate must then be ground into the body in a ball mill. It may also be introduced into a body in a blunger but this practice is not as satisfactory.

In conclusion the writers wish to express their appreciation to Mr. A. V. Bleininger for advice in outlining the work and to the force of the Clay Products Division of the Bureau of Standards for a great deal of assistance in carrying on the experimental work.

[1] For complete description see G. H. Brown, "Burning of Porcelain," Proceedings New Jersey Clay Workers' Association, 1914.

THE USE OF CAR TUNNEL KILNS FOR BRICK AND OTHER PRODUCTS OF CRUDE CLAYS.

By Ellis Lovejoy, E.M., Columbus, O.

There are a number of problems in car tunnel kilns which must be solved in order to adapt the kiln to common clay products.

A major problem is to distribute the heat uniformly among the ware. The ware is in relatively small units but each unit comes in close contact with the furnace.

In large down-draft kilns the ware placed around the bags where the flame strikes it is largely rejected or at best it goes into second quality or culls. There would exist the car tunnel kiln problem in down-draft kilns if the kilns were built four to six feet wide with the bags removed and the ware set in small units in front of the furnaces. We would have then about one thousand bricks with a furnace on each side. How many of the bricks would be fire-flashed and overburned? Suppose we are burning face bricks, what percentage of product with uniform or satisfactory color would be obtained? Color is a very sensitive test of combustion conditions. Paving bricks are also very sensitive to heat conditions. Many factories cannot produce No. 1 quality bricks around the bags and over the top of the kiln, but in a down-draft kiln the percentage of these second quality bricks is relatively small. What would be the result if fifty or more per cent of the product is exposed to the flame?

Pottery, in the manufacture of which the car tunnel kiln is making rapid progress, is placed in saggers and the walls thereof interpose between the flame and the ware. Moreover, the size and shape of the saggers are such as to provide large spaces for the circulation of the air and gases. In some operations it is customary to set bisque on top and glost at the bottom, thus taking advantage of difference in temperature, and such difference in temperature is not serious.

Bricks, however, are set in close checker work and it is difficult to distribute the heat uniformly through the mass.

We cannot set bricks vertically around the tops of the bags in down-draft kilns because the greater shrinkage on the flame face will cause the face to draw over and fall into the bags, followed by a second and a third face as they become exposed to the flames. We must, therefore, rack back the bricks on cars as we do around kiln bags, and if we do this where are we to get any high-grade face bricks which must be perfectly faced in the setting? Some hollow tiles made from high shrinking and low burning range clays are badly warped and misshapen where the flame strikes them and the loss of ware would be serious if the flame struck the bulk of the mass.

Any cull brick pile will contain bricks much smaller on one end, due to the fact that the small end was exposed to flame, as in the arches of up-draft kilns. Under such conditions there is a marked difference in color, size, and hardness in eight inches in length. Would the conditions in a car tunnel kiln be equivalent to those in the arches of an up-draft kiln?

In three designs of car tunnel kilns the combustion takes place in a box or flue on each side of the kiln and the heat conducted through the walls of the flues is carried to the ware by circulation of air around the combustion flues thence over and down among the ware. In two kilns the operation is regenerative—the air after passing among the ware re-circulates around the combustion flues. In two other designs the operation is that of a down-draft kiln in which the combustion gases rise through a bag and descend among the ware and are drawn through a perforated floor into the next compartment and continuing until finally drawn from the kiln. In the other designs the cars of ware simply pass a flaming furnace sometimes with an intervening flash or perforated wall. There are then three types of car tunnel kilns—direct heating, indirect heating in the tunnel, and compartment operation.

One direct-heating type sets a combustion arch transversely of the car in the bottom of the ware comparable with the arch in an up-draft kiln and this arch, being built of fire bricks and retained as a permanent part of the car furniture, should give better results than those from the arch of an up-draft kiln. The indirect-heating types would seemingly better solve the flame

difficulty, although the compartment type appears advantageous and may prove very efficient when it is successfully developed and adapted. Unfortunately, one of the compartment type was not successful in an initial installation, but one must not conclude that the type is not promising because of this single failure.

There have been many failures of the direct-fire tunnel types in the past, yet new designs are constantly coming and proving successful in some lines of ware.

Manufacturers of common wares will have to be shown that simply pushing cars of ware through a fiery furnace will give satisfactory results:—namely, freedom from fire-flashing; uniformity in color, size, and hardness; no warping and no fire-cracking.

Assuming that the flame difficulty may be overcome in some types of kiln, there remain the racking back, complex bonding to insure the stability of the mass of ware and to provide circulating flues.

Such setting is serious in face brick manufacture and may be objectionable in other common wares. Drain tile, for instance, does not lend itself readily to complex setting, and it is not desirable to have transverse or longitudinal flues in the ware.

The manufacture of common wares is regarded by many ceramists as a job requiring little intelligence, but as a matter of fact the common ware manufacturer has to overcome the most difficult problems. He is dealing with a single raw clay with all its inherent difficulties which must be overcome in a large way in every step of the process of manufacture, while the manufacturer of other wares is dealing with a synthetic body and is incompetent if he cannot improve on natural clays.

One of the problems in a car tunnel kiln is to protect the cars from the heat. Sand seals on the sides and tongued and grooved end-locks in the car frame, or furniture, shut off the cars from the heat tunnels fairly well but not perfectly and they do not overcome conduction. Two designs do not even use sand seals and the car simply projects into a recess in the side wall, at best offering but slight resistance to the upward passage of air. In practically all designs there is some method of cooling the under tunnel and thus protecting the cars. One cools the cars by air pipes along the tunnel walls adjacent to the car structure. This

is an indirect way of cooling by means of which there is theoretically no air circulation in the tunnel under the car floor and the only air which could get into the upper tunnel from the car space would be that from leakage. Another design has a duct under the cars which may be closed and the only air admission is that from leakage. Dampers in the bottom of this duct may be opened and any amount of air allowed to enter. The amount of air which is allowed to enter is that required to keep the cars cool, and this air circulates around the car structure and rises into the heat tunnel, there being no sand seal. A third design introduces the air under pressure through pipes and jets the air against the car structure at intervals in the hot zones. Again we have direct provision to draw the air through the car duct and deliver it under the furnace grates or to the gas burners, usually a free circulation under the cars but in one instance through a sheet metal casing, thus cooling the cars indirectly.

It matters not how it is accomplished, the cars must be cooled and there is more or less air finding its way up around the cars and enveloping the ware.

Let us consider a down-draft kiln in this light. Suppose we circulate cold air under the kiln floor and allow it to seep, or freely flow, into the kiln on the inside of the wall at the floor level. Every down-draft kiln burner knows, or should know, that chilling the kiln bottom results in serious loss in the bottom ware. A prominent company several years ago put flues under the kiln floor through which air was to be taken from the outside, under the kiln floor, heated by conduction from the waste combustion gases, then back to the furnace for primary combustion. The purpose was to heat the air for combustion which it accomplished, but at the same time cooled the kiln bottom to the extent of serious effect on the ware and the scheme had to be abandoned, as have several other similar schemes.

Dampness under the kiln has the same cooling effect on the kiln bottom in consequence of evaporation and many manufacturers have experienced trouble and losses on this account. Common wares cannot be burnt satisfactorily in either down-draft or continuous kilns if the kiln floor is chilled and, particularly with some short-burning range clays, the effect would be to quickly

put a profitable business into the hands of a receiver with an ultimate sale of the plant for junk.

The car tops are cooled and the best of insulation is not the equal of a blanket of high temperature combustion gases under the kiln floor. In the combustion zone we have in the direct-fire kilns combustion gases rising in the space between the ware and the flash wall of the furnace. We also have a current of cold air from under the cars creeping up the face of the ware, taking heat from the bottom ware and carrying it to the top and finally commingling and combining with the furnace gases in secondary combustion, thus still further increasing the temperature on top.

There are many clays, particularly limey clays, and some vitrified products, which cannot be profitably burned if the variation in kiln temperature exceeds 60° C, —three cones. This can be done commercially in down-draft kilns. We say "commercially" with a purpose. There can be obtained the same cone temperature in top and bottom of a down-draft kiln but at such fuel expense as to rule it out as a commercial operation. What can be done commercially in a car tunnel kiln? Certain reports indicate the same temperature throughout the mass of ware. This sounds encouraging indeed, but is it true? The manufacturers of crude clay wares wish to know and are greatly interested. There are also reports that common ware on the face of the cars is vitrified, or at least extremely hard, while that in the bottom center is barely within the limit of salable building bricks. This does not check with reports previously mentioned. Some kilns are burning all biscuit and others all glost, but what variations in temperatures will these wares stand? One kiln, at least, burns bisque on top and glost in the bottom to take advantage of the difference in temperature.

L. E. Barringer[1] states that, "the kiln at Schenectady is used in firing porcelain insulators to a temperature of 1300 to 1400° C." A variation of 100 degrees in a four-foot column of common ware in many instances is prohibitive.

It is frequently necessary to get within 60 degrees in a ten-foot column of ware, and it is desirable to do better. Even this variation, in a four-foot column, would give too much difference in

[1] *Trans. Am. Ceram. Soc.*, **18**, 118 (1916).

color, size, and degree of vitrification to be satisfactory. In effect, the product would be practically all "bag" bricks, since we cannot encase our common wares in saggers.

Common wares are often quite wet when set in the kilns. They should not be, of course, but they are, and in consequence require careful water-smoking, which is particularly true of dry-pressed bricks requiring from three to eight days of slow water-smoking. Will the car tunnel kiln be adapted to this product?

Many common clays are high in carbon and iron sulphide, as for example the black lignitic clays in New Jersey and the black Ohio shale. The oxidation of these is a serious problem. How will it be worked out in the car tunnel kiln?

One might assume that we are opposed to the car tunnel kiln, but, quite the contrary, we are very much interested in its success and when we are shown that it will advance the manufacture of common clay wares, we will boost it to the limit.

The car tunnel kiln is a century old and more, and there are many wrecks strewn along the wayside. In the present revival, the kiln has come to stay, but there are a number of problems which must be solved to adapt it to the successful production of common clay wares.

We have not a complete list of the car tunnel kilns in this country, but there are over forty under construction, in operation, or abandoned.

So far as indicated by available records there are fifteen under construction and in operation on white-ware, porcelain, etc.; there are five burning refractories; two on building bricks; seven abandoned as failures. There are also several in other industries, —burning carbons, annealing, etc., about which we have no information.

There are more than a dozen kilns in this country devised by different inventors, from which the clay workers may choose. Of these, at least ten have been tried out, or are under construction. Two types have the credit of twelve or more kilns each in this country. This shows the marked interest in the car tunnel kiln.

The kiln is rapidly being given the opportunity to prove its merits, but much remains to be done to adapt it to the several

distinct lines of ware before it can take its place alongside of, or displace, the other types of continuous kilns.

COMMUNICATED DISCUSSION.

L. E. BARRINGER: The author has clearly pointed out some of the difficulties which might be anticipated in attempting the use of continuous tunnel kilns in the burning of products made from crude clays, as structural and paving brick, drain tile, etc.

The first criticism which is made is that of possible lack of a sufficiently uniform temperature in the continuous kiln and the difficulties of properly distributing the heat through the ware as the latter passes through the combustion zone. It is pointed out that the nearness of crude clay wares to the throats of the fire boxes in all types of kilns leads to fire-flashing, overburning and shrinkage differentials, and it is the author's opinion that a very much larger percentage of the product would be subjected to overfiring, through nearness to the fire boxes, than in the large periodic (and principally down-draft) kilns commonly employed for the firing of the crude clay wares.

Exposure to the direct flame of the furnace is of course productive of high losses and the author's question as to what would be the result if 50 per cent or more of the product should be exposed to the flame, might be answered by saying that the result would probably be a loss of high-grade ware to the extent of 50 per cent or more. But there should not be such a high percentage of ware exposed to excessive temperature and I believe that the distribution of temperature can be controlled within closer limits in a properly designed tunnel kiln than in a large periodic down-draft kiln.

Unfortunately, my statements[1] of temperature distribution in connection with the tunnel kiln in use in the Porcelain Department of the General Electric Company were perhaps not made sufficiently clear. In the paper in question it was stated that "the kiln at Schenectady is used in firing porcelain insulators to a temperature of 1300 to 1400° C" which was intended to mean that the maturing temperature of porcelain was always between these limits, that is, some porcelains were fired at a little higher

[1] *Trans. Am. Ceram. Soc.*, **18**, 118 (1916).

temperature than others. A little later in the same paragraph, however, the statement is made "a uniformity of distribution of temperature is secured of well within one cone." This means that whether the porcelain is fired at 1340° C or 1380° C, the actual differential at the proper maturing temperature can be reduced to within 20° C. For instance, if the maturing temperature is 1340° C, the temperature in all parts of the firing zone of the continuous kiln can be maintained within the limits 1330 to 1350° C.

In the same paper the writer made the statement that for brick and crude clay wares, the necessity of uniform temperature is not as great as in the higher-grade clay wares, since matters of porosity, exact size and uniform color are not as important. I think the author of the paper under discussion confirms this in stating that there are many common clay products which cannot be profitably burned "if the variation in kiln temperature exceeds 60° C (3 cones)." This is decidedly more than the one cone or 20° C which is required in the firing of such ware as electrical porcelain and which is maintained in the tunnel kiln being operated at Schenectady.

There would seem to be no fundamental reason why the crude clay wares cannot properly be protected from fire-flashing and over-burning in a continuous tunnel kiln if the fire boxes and fire zone are properly constructed. Inasmuch as the temperatures required in firing brick and similar products are not as high as those necessary for the firing of porcelain, the fire boxes can be placed at a greater distance from the tunnel of the continuous kiln at the firing zone without excessive loss of heat.

A second point that the author brings out is the uncertainty of being able to regulate the condition of the fire gases and to bring about oxidizing or reducing conditions as required. This, however, can be done, although it must be admitted that a continuous kiln from its very nature cannot be as quickly manipulated in this respect as a periodic kiln and the changes from a reducing fire to an oxidizing fire or *vice versa* require longer periods. Such control can be obtained, however, either in the open tunnel kiln, as the Didier-March, or in the muffle kiln, as the Dressler.

In discussing the matter of protecting the cars by sand seals

and otherwise, and in considering the possibility of air leakage which should tend to cool the floor or bottom of the kiln, the author fears that such cold air leakage will materially affect the temperature of the ware at the bottom of the kiln. In this connection, however, it is to be pointed out that the very point where such air leakage might take place is at the point of maximum temperature, that is, between the face of the ware and the ports from the fire boxes, so that slight air leakage might possibly do more good than harm. Of course, if such leakage is excessive, it may be injurious, both to the under-structure of the car and to the ware upon the car. If the writer understands the paper correctly, however, the direction of cold air leakage is considered as upward, whereas designers of kilns with sand seals undoubtedly assume that the leakage will be downward into the subway beneath the cars and the sand seal is particularly necessary to prevent the under parts of the car becoming so overheated that they are not as readily operated, to say nothing of the rapid deterioration of the iron and steel under such conditions.

It seems to the writer that of the difficulties which have been pointed out by Mr. Lovejoy, the most troublesome to meet successfully would be (*a*) the proper "water-smoking" of crude clay wares, (*b*) the handling of highly carbonaceous, calcareous and pyritic clays, and (*c*) the control of kiln gases, within sufficiently short time periods.

The designers and builders of continuous car tunnel kilns will probably desire to discuss the proper construction and method of handling such kilns when the burning of crude clay ware is involved and to answer some of the pertinent inquiries which Mr. Lovejoy has made.

General Electric Co.,
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THE PRESENCE OF IRON IN THE FURNACE ATMOSPHERE AS A SOURCE OF COLOR IN THE MANUFACTURE OF OPTICAL GLASS.

By Edward W. Washburn, Urbana, Ill.

It is well known that the presence of very small quantities of iron in glass imparts to it a greenish color. In the common varieties of glass, this color is usually eliminated by employing a "decolorizer" which produces the complimentary color. However, this procedure is not possible in the case of optical glass owing to the decreased transmission of light which accompanies it. For this reason each material employed in making up the batch for producing optical glasses must have an extremely high degree of purity as regards its content of iron.

The coloring effect of iron seems to be especially pronounced in the case of the flint glasses, and the glasses of this type hitherto manufactured in this country for optical purposes all have a very evident greenish tinge and this in spite of every precaution to employ only the purest materials. The writer's attention was first directed to this situation by the results obtained with some experimental melts of a heavy flint glass ($n_D = 1.64$) obtained in an electric furnace. These melts were entirely free from any trace of color, although the same batch when melted in the same type of pot in a gas-fired furnace invariably gave a product having a decided greenish color.

The pots in both cases were kept carefully covered during the melting and the other conditions in the two experiments were such that the only possible source for the color obtained with the gas-fired furnace seemed to be the presence of iron in some form in the atmosphere of the furnace. An opportunity to further test this hypothesis was afforded the writer by Mr. A. V. Bleininger, of the Bureau of Standards. The tests were made on one of the large pot furnaces of the Bureau's optical glass factory at Pittsburgh and were conducted in the following manner:

A five-foot fused silica tube, open at both ends, was inserted

through the wall of the furnace so that the end of the tube was immediately above the pot of melted glass. The temperature of the furnace was approximately at the maximum point attained during the manufacturing operation, and was just immediately preceding the period at which stirring was begun. The outer end of the tube was connected to a glass tube ending below the surface of a dilute solution of sulphuric acid contained in a wash-bottle. Suction was applied to the wash-bottle so as to draw a stream of the furnace gas through the sulphuric acid. The experiment was continued for two hours, at the end of which time the silica tube was removed and washed thoroughly on the inside with some of the sulphuric acid from the wash-bottle. The acid was then tested for iron in the usual way with a solution of ammonium sulphocyanate, and a distinct positive test was obtained.

This experiment clearly demonstrated the presence of iron in the furnace atmosphere and rendered it extremely probable that this constituted a significant source of the color in the glass. This was further confirmed by the fact that, previous to stirring, a sample of the glass removed from the pot had a much better color than was the case after the pot had been stirred for a number of hours. Evidently, the iron taken up from the furnace atmosphere was mixed throughout the glass by the process of stirring.

The iron in the atmosphere was doubtless present in the form of ferric oxide, but whether the oxide was present in the form of a fine dust or in the form of vapor was not definitely determined, although it seems reasonable to believe that at the temperatures attained in the furnace, ferric oxide might have a sufficiently high vapor pressure to produce the observed results. However, it is hoped to settle this question definitely by attempting to directly measure the vapor pressure of ferric oxide at high temperatures.

Two obvious sources for the iron in the furnace atmosphere were: (1) The iron burners which extended far enough into the furnaces so that the ends were covered with a coating of the oxide; and (2) the iron content of the fire-brick lining of the furnace. In order to remove these two sources of contamination,

the iron burners were replaced by burners made of clay and the interior walls of the furnace were covered with a coating of kaolin. As a result of these changes in the furnace, Mr. A. E. Williams, Superintendent of the Pittsburgh Optical Glass Plant, reports that a distinct improvement in the color of the heavy flint glasses has resulted.

It was noted that the layer of white kaolin which was placed on the interior walls of the furnace gradually acquired a red color, either by the absorption of iron from the brick behind it or by the taking up of iron from the furnace atmosphere.

The results of the above experiments demonstrate very clearly that in the construction of furnaces for the manufacture of optical glass it is highly desirable to exclude all materials which will give up iron to the atmosphere of the furnace. The interior of the furnace should, if possible, be lined with a course of kaolin bricks, and if it is necessary to employ any object constructed of metallic iron for any purpose *in the interior* of the furnace, water cooling should be employed to prevent volatilization of the iron.

DEPARTMENT OF CERAMIC ENGINEERING,
UNIVERSITY OF ILLINOIS.

THE CONTROL OF THE LUSTER OF ENAMELS.[1]

By Homer F. Staley, Washington, D. C.

Crystallization.

When melted, glasses are true solutions, corresponding in all respects to solutions of salts and water at ordinary temperatures. When these molten solutions are cooled, we would expect them to turn gradually to a mass of crystals, just as an aqueous solution of salt does if the temperature to which it is cooled is sufficiently low. The only difference is that the glassy solutions should crystallize at higher temperatures. The temperatures at which glasses would become completely crystallized, if sufficient time were allowed, vary from 550 to 1100° C, yet in practice they are cooled and exist permanently at atmospheric temperatures without any crystallization taking place. In this condition they are still true solutions—differing from aqueous solutions only in being so viscous that they are rigid. All bright finish enamels, glasses and glazes may be regarded then as undercooled liquids. The tumblers from which we drink are in a sense just as truly liquids as the water they contain.

Of course, if the constituents of a glass crystallize, the surface becomes mat instead of bright. Since bright finish enamels are the type desired for enameling metals, the enamel maker must so compound his enamels that they will not crystallize when subjected to the normal working and cooling conditions of enameling shops. Fortunately, the sudden cooling to which enameled ware is subjected is not favorable to crystallization. On the other hand, the working temperature is so low that the glass is easily saturated by the compounds formed in the molten magma by some of the oxides used. Just as a hot, saturated, aqueous salt solution tends to become supersaturated and to deposit crystals of the salt on cooling, just so does a hot, saturated glass or enamel solution tend to deposit crystals when it is cooled.

Effect of Viscosity.

The most simple method of overcoming the tendency to crystal-

[1] By permission of the Director, Bureau of Standards.

lize is to make the enamel viscous at the temperatures at which crystallization takes place. In even a moderately viscous liquid, it takes considerable time for crystallization to start and the rate of growth is slow. Since enameled iron ware is cooled so rapidly, sufficient time is not given in the cooling process for an appreciable formation of crystals in a viscous enamel, unless the tendency for deposition of crystals is very great.

Silica alone melts to a very viscous glass, and, in general, the addition of silica to any melt increases the viscosity. Silicates high in silica also melt to viscous glasses. If silica (flint), sand or feldspar (a high-silica compound) is added to an enamel, the glass is rendered more viscous at all temperatures, and the tendency to become dull from crystallization is lessened. Since the working temperature of the enamel is raised by this procedure, this method has but slight application in controlling the viscosity of enamels that must mature at temperatures rather rigidly fixed by shop practice and working conditions.

Boric oxide alone forms a very viscous glass at low temperatures; but, as shown by the writer,[1] the viscosity decreases rapidly as the temperature rises. The glass was found to be three times as viscous at 750° C as it was at 1000° C. The first temperature approximates that at which crystallization takes place in enamels, and the second is near the maturing temperature of most enamels for cast iron. The borate glasses of any given base resemble silicate glasses in behavior and become more viscous as the percentage of boric oxide increases. The following results were obtained for barium oxide—boric oxide glasses:

Per cent B_2O_3.	Per cent BaO.	Relative viscosity at the same temperature.
20	80	3.05
25	75	3.18
30	70	3.35
35	65	3.52
40	60	3.70
45	55	4.02

It is noteworthy that the presence of compounds and eutectic compositions produced no noticeable effect on the viscosity curves.[2]

[1] "The Viscosity of Molten Glasses," Original Communications, *Eighth International Congress of Applied Chemistry*, **5**, p. 127.

[2] Cf. *Trans. Am. Ceram. Soc.*, **13**, 675 (1911).

The viscosity of borate glasses decreases with rise of temperature in the same general way as that of fused boric oxide, but not as rapidly. The effect of increasing the boric oxide in cast iron enamels is to increase the viscosity at the temperatures at which crystallization is liable to take place, and thus to decrease the tendency to matness. Its effect differs from that of silica in that the maturing temperature is not raised but, in the case of many enamels, is actually lowered.

Kaolin (china clay) has a very decided tendency to raise the viscosity of enamels but is not much used in American although found in some German formulas. Any material which does not fuse or go into solution in the enamel, such as most metallic oxides added as opacifiers, makes the enamel more viscous. Decrease of any of the fluxing oxides, except boric oxide, makes the enamel more viscous. Therefore, viscosity may be increased by decreasing any of these. Decrease of fluorides has the same effect.

Effect of Concentrations.

With the exception of boric oxide, all of the materials in enamel compositions known as fluxes, *i. e.*, the oxides of lead, zinc, sodium, potassium, calcium, barium, magnesium, and the various fluorides, tend to form compounds which are easily crystallizable. Lead oxide differs from the others in that its compounds when melted alone do not crystallize until very low temperatures are reached. Lead silicates do not crystallize until temperatures of 750° C or lower are reached,[1] and lead borates have even lower crystallization temperatures. Since normal enamel compositions are too viscous at low temperatures to allow crystallization to take place, lead compounds do not crystallize from enamel glasses. Therefore, lead oxide shares with boric oxide the distinction of being a flux and yet not producing a mat finish when present in the enamel composition in large amounts.

Of course, the tendency for any compound to separate in the crystalline form from a cooling glass is decreased by decreasing the amount of the compound in the glass. Therefore, the amount of each of the fluxes, except boric oxide and lead oxide, should be kept low. This means that as the total amount of these crystal-forming fluxes increases a greater variety must be used.

[1] Cooper, Shaw and Loomis, *Am. Chem. Jour.*, **1909**, p. 461.

The effect of concentration of various fluxing oxides is shown by the series of enamels described below. As the basis of the series, the following batch was taken:

Raw.	Melted Percentages.
	26.5 silica
Potash feldspar.....41.0	7.5 alumina
	7.0 potassium oxide
Borax.....24.6	9.0 boric oxide
Sodium nitrate..... 2.7	5.0 sodium oxide
Cryolite.....12.0	4.8 aluminium fluoride
	7.2 sodium fluoride
Tin oxide..... 8.0	8.0 tin oxide
	75.0 constant
	25.0 variable
	100.0

The composition of the 25 per cent variable part and the luster of the resultant enamels is indicated in the accompanying table:

TABLE SHOWING EFFECT OF COMPOSITION ON LUSTER.

Number.	Na_2O from soda ash.	BaO from barium carbonate.	CaO from calcium carbonate.	ZnO from zinc oxide.	PbO from red lead.	B_2O_3 from boric acid.	Luster.
1	25						mat
2		25					semi-mat
3			25				not melted
4				25			mat
5					25		bright
6						25	bright
7	12.5	12.5					semi-mat
8	12.5			12.5			mat
9	12.5					12.5	semi-mat
10		12.5		12.5			semi-mat
11		12.5				12.5	bright
12				12.5		12.5	bright
13	8.33	8.33		8.33			oily
14		8.33		8.33		8.33	bright
15	5.00	8.33		8.33	3.33		bright
16	5.00	8.33		8.33		3.33	bright

Enameling Technique.

Any necessity for prolonging the enameling operation that involves partial cooling and reheating of the enamel after the coat is matured furnishes favorable opportunity for the development of crystallization and dull finish. Therefore, considerable care must be taken to avoid all necessity for patching by having the metal in the best possible shape for enameling before the operation commences, and by employing the most skilful workmen to apply the enamel.

Sulphur Compounds.

It is well known that sulphur compounds in an enamel tend to separate on the surface in feather-like crystals, causing a diminution of luster. While this may be due to sulphur in the enamel materials, and the presence of sulphur in these should be avoided, it is not probable that enamel compositions made from the grade of chemicals commonly employed contain enough sulphur to cause the trouble. Seger has shown that a glass can contain 2 to 4 per cent of sulphur trioxide and still be perfectly clear.[1] It is interesting to note that when Seger made a melt from sodium carbonate, barium sulphate and silica, the glass gall, which separated when an excess of sulphur was present, consisted of sodium sulphate, not barium sulphate as might be expected from the strong affinity of barium for sulphur at low temperatures. In fact, glass gall from common glasses ordinarily consists largely of sodium sulphate. Mellor[2] records experiments in which ordinary pottery glazes were found to dissolve comparatively large amounts of various sulphates, such as those of barium, calcium, lead, sodium, and potassium, without showing any ill effects. An experienced enamel mixer informs me that he once had a separation of sodium sulphate in the form of glass gall in considerable amount from an enamel batch in the melting tank. In grinding this batch he mixed the glass gall with the good glass and got satisfactory ware from the mixture. Mellor believes that the feathering of pottery glazes by sulphur is due to the satura-

[1] "Collected Writings of Herman A. Seger," p. 646. Published by Am. Ceram. Soc.

[2] J. W. Mellor, "Clay and Pottery Industries," Vol. 1, p. 63, published by Chas. Griffith and Co., London.

tion of a surface film of the glaze by sulphur in the kiln atmosphere. This is probably the case in enamels also, for it occurs most frequently when a sulphur-bearing fuel is used for heating the enameling furnaces. A number of enameling plants experienced difficulty from sulphur feathering when they changed from the use of natural gas to bituminous coal. The trouble is much less common when well-ventilated muffles are used than when the air currents in these are sluggish. Cracks in the floor of the muffle which allow the products of combustion to leak in are a common cause of sulphured ware. Open-arch or semi-muffle kilns are prone to produce ware of poor gloss unless a strong draft is used so as to keep the flame hugging the roof of the furnace.

Sometimes quicklime is placed around the inside of the muffle against the walls, in the hope that the quicklime will absorb the sulphur. This is generally not very effective. In the first place, it is only rarely that the sulphur-bearing fumes pass through or over the quicklime unless it is placed directly over a crack or hole. The lime does not attract the sulphur from the kiln atmosphere as a whole. In the second place, if sulphur-bearing fumes do come in contact with the lime, it soon becomes saturated and should be replaced much more often than is the common practice. One per cent of volatile sulphur in a ton of coal will give 40 pounds of sulphur dioxide or 50 pounds of sulphur trioxide, either of which will neutralize 35 pounds of quicklime if brought into intimate contact with it. It sometimes pays to pile quicklime over a temporary patch in the floor of a muffle, but even then the lime should be changed daily.

Index of Refraction.

Aside from the question of glasses being dulled by the presence of crystals or sulphur compounds on their surfaces, the brilliance of the glasses themselves will vary. The brilliance of a glass is measured by its refraction for light, the higher the index of refraction, the more brilliant the glass. In any one class of glasses, the index of refraction is higher the greater the density of the glass.[1] Since lead oxide, barium oxide and zinc oxide tend to

[1] H. Hovestadt, "Jena Glass," pp. 388–393, published by The Macmillan Co., New York.

produce very heavy glasses, they also produce glasses of great brilliance. Potassium oxide makes more brilliant glasses than sodium oxide, and the substitution of boric oxide for silica makes more brilliant glasses, although the density of the glass is lowered slightly. High-flint enamels are generally more brilliant than those in which feldspar is the only refractory.

COMMUNICATED DISCUSSION.

E. P. POSTE: We were very much interested in the remarks under the heading "Sulphur Compounds," in which Mr. Staley has referred to the presence of sodium sulphate on the surface of enamels, introduced by sulphur in the raw materials entering into the enamel mixture or by sulphur gases in contact with the enamel during burning.

We have carefully studied this particular type of trouble under two different sets of circumstances in connection with steel enamels applied by the wet process.

The first instance came to our attention while endeavoring to work, on a semi-commercial scale, an enamel which, through the experimental stages, had been very difficult to bring to a proper condition for spraying. The clays which were in use in "setting up" commercial formulas at that time did not properly suspend the enamel in question—without the addition of an amount which caused a definite dullness of the surface. Using less clay, it was necessary to add such an excessive amount of magnesium sulphate solution as a vehicle that a very definite sulphur scum was produced.

The other instance in mind came to our notice while we were endeavoring to burn commercial formulas on an experimental scale in a small furnace which was being fired by producer gas under conditions such that the products of combustion came in contact with the enamel. This took place at a time when it became necessary to find a substitute for natural gas in firing a direct-fired enamel furnace. The natural gas had never given trouble from sulphur scum. The first producer gas used was made from a coal which contained 2.79 per cent sulphur and the second test was made with a gas made from a coal containing 0.77 per cent sulphur. In both cases there was a very definite sulphur

scum which did not appear immediately on cooling but which was very evident after 24 hours.

It is particularly interesting to note that in the several cases of scumming—due to magnesium sulphate and the producer-gas fuel—the sulphur scum was carefully tested and identified as sodium sulphate, a fact which confirms very definitely the statements of Mr. Staley and of the other authors to whom he refers.

THE ELYRIA ENAMELED PRODUCTS CO.
ELYRIA, OHIO.

OBSERVATIONS ON APPARENT CAUSES OF FAILURE OF LEAD GLASS POTS.[1]

By A. F. Gorton.

Introduction.

In order to appreciate the difficulty of building a satisfactory pot for melting lead glass, it is necessary for one to examine a number of pots after removal from the furnace, and to see for himself the many ways in which failure is possible. When one considers the unusual physical and chemical strains that a pot must withstand, it seems remarkable that more than a single melt is obtainable, yet 15 to 20 melts is only an average life, and even now, three years after the disappearance of the lamented German clay, records of 40 to 60 melts are occasionally encountered. A pot must be heated with intelligent care in the arch, or preheating furnace, and this by the way is no mean task when one considers the rather crude design of the arch, the inability to distribute the heat properly, and the constant temptation to hurry the pot into the furnace for the sake of maintaining production(!); secondly, the pot must be transferred to the furnace, and this cannot be accomplished under present-day methods without subjecting it to a certain amount of strain, partly mechanical and in part thermal. Once in the furnace, the pot is subjected to both physical and chemical strains: (1) the throwing in of the relatively cold (and sometimes damp) batch is a distinct shock, and must result in the formation of tiny surface cracks in the bottom, which widen as the glass works into them; (2) there is an erosion of the clay due to the boiling action and wash of the molten glass; (3) the hydrostatic pressure of the glass charge is sometimes sufficient, during the melting period, to cause the side walls to bulge outward or "belly." These are physical actions. The actual corrosion of the clay by the glass and especially the slagging action of iron may be cited as chemical causes of leaks in pots.

[1] Read at the meeting of the Northern Ohio Section of the American Ceramic Society, Cleveland, O., December 9, 1918.

While inspection of pots after they are hauled out of the furnace usually affords some ground on which to base an inference as to the probable cause or causes of failure, there are many phenomena noticed, at times in only one pot out of 20, at other times in a succession of pots, which baffle the combined efforts of glass-house manager and potmaker to clear up, and remain a puzzle. The discussion that follows is based upon the writer's observations and impressions gained in the examination of the remains of some used pots which were broken up under his personal direction at the Toledo plant of the Libbey Glass Co., and though the limited number of pots precludes any numerical generalizations as to the causes of failure, still it will serve as a satisfactory illustration of the types of failure commonly observed. Twenty-two pots in all were inspected, and it was found that the general defects could be listed as follows:

1. Pitting and corrosion of the bottom, resulting, in a majority of cases, in a leak at one point or another—particularly marked at the knuckle (or intersection of the walls with the bottom).

2. Cracking of the bottom, with no sign of corrosion save in the jaws of the crack. (It seems that the glass does not attack the bottom unless the smooth surface is broken through and the porous clay of the interior exposed.)

3. Crack in the side, extending clear through, causing escape of the glass.

4. Side walls scored or furrowed from metal-line down. This action probably starts from a rather deep crack.

5. Hole through the side. It may be found on either side, about twelve inches or more above the bottom. Horizontal openings, especially near the bottom, are not herein included.

6. Sides bulged. In some instances the pot is strained at the bulge to such an extent that a crack develops, letting the glass escape; at times a rip in the back accompanies the bulging. If the clay is not sufficiently refractory, the pot will squat or collapse, and this condition was not uncommon some years ago, when the necessity of seeking new mixtures of raw clays and new proportions of clay to grog was forced upon the potmaker.

7. Hole through the back. This occurs sometimes at a height of 12 to 15 inches, at times much lower.

8. Crack through the back. These cracks, like those in the side, are always vertical.

9. Cracking under the hood, resulting in a leak. This fault was noticed in 4 of the 22 pots, and is not altogether to be laid to carelessness on the part of the potmaker, as a mechanical strain is unavoidable at this point, due to the construction of the pot, which is not lessened by the fact that the hood is the coolest part of the pot in the furnace.

10. Cracking and caving in of the crown. The construction of the pot-furnace is such that the heat strikes against the crown and back of the pot. The temperatures reached at these points are undoubtedly as high as 2700° F., as the clay is often blistered (overfired) on the surface, and beneath the surface has reached a glassy or "vitrified" stage. There is a gradual change in color from the back wall to the bottom, the black shading off into a reddish buff, and this into a very pale buff or cream color in the middle of the bottom. Corresponding to this change in hue there is a change in porosity, for the parts described, from 5 per cent to 25 or 28 per cent. From the value of the porosity, it is quite easy to calculate the maximum temperature attained at the point in question, after the temperature-porosity curve has been determined experimentally for the pot-clay. The effect of this severe heat is to flatten the crown, but it rarely causes a collapse. Cracks in the crown result probably from strains set up in drying the pot. The crown, being the thinnest portion of the pot (2 to 3 inches as compared with $4^1/_2$ inches in the bottom and walls), dries most rapidly, and, it seems, also cracks most readily. Then, too, it is hard for the potmaker, in shaping the crown, to pack the clay as firmly as in the case of the walls, upon which he can exert the unimpeded strength of both hands.

From glass-house reports covering a period of several months or a year, it is possible to gain an idea as to which types of failure are most frequent. The writer has gone over reports from the Libbey Glass Co. for the four months June–September of this year, in which a total of 379 pots are listed, and finds that 81 per cent broke in the bottom, 11 per cent in the side, and 6 per cent in the back. Of the 22 pots above referred to, 18 broke in the bottom,—or a percentage of 81—two in the back, and two in

the side. The agreement of the percentage of bottom breaks is a coincidence, but it shows clearly how the vast majority of pots fail. In the following discussion an attempt will be made to give the various possible causes of such leaks, with a view to explaining the difficulty, under present-day glass-house procedure, of remedying these defects through alteration of the ingredients or the proportions of the pot batch.

Bottom Leaks.—Taking up first the case of bottom leaks, it was noticed that 8 pots failed through cracking, and 10 through corrosion. Of the former, two gave one melt each and one gave no melts. In the last case there were two cracks running from front to back, exactly over the points where the pot is supported by the fork, when it is brought from the arch to the furnace, hence the explanation is evident. Since only one of the 8 pots was of long life (28 melts), it seems likely that cracking in such cases is due to strains set up (1) in drying the pot, (2) in the preheating period, (3) in transferring it to the furnace. As to the first cause, it may be stated that when the bottom cracks open in drying, the direction of the crack is always from side to side, *i. e.*, at right angles to the length. The writer, where possible, noted the direction of the cracks in the broken pots, and in the majority of cases they ran from front to back. This applies only to long cracks. Jenkinson and Marson,[1] from observations made at the works of the Edinburgh and Leith Flint Glass Co., Edinburgh, state that insufficient preliminary burning in the arch may result in a sudden shrinkage after setting in the furnace, and as the bottom is much cooler than the sides, owing to the conductivity of the bench supporting the pot, the excessive shrinkage of the walls may force the bottom upward into a concave shape, and thus crack it. While the writer has seen no trace of this trouble, it may be well to point out the possibility of a different source of trouble: distortion of the bottom by an uneven bed. This also was not noticed in the present work, as the bottoms of all of the pots were plane.

Corrosion.—Turning to the next point under discussion—failure of pots due to corrosion—mention was made of the fact that 10 pots of the 18 showed corrosion distinct from that which

[1] *J. Soc. Glass Tech.*, Sept., 1918, p. 175.

accompanies a mere crack. That is, an appreciable volume of clay had disappeared, mostly from the bottom. These pots had given from 2 to 67 melts, which is surely the extreme range of life. In 8 pots of the 10, close scrutiny revealed the presence of iron, which had worked into the crevices, slagging the clay and opening the way for the leak. It was also noticeable in the form of very dark green or black glass lining the sides of the hollow or crack. Invariably the iron found the lowest point in the bottom. This was true also of metallic lead, which occurred in only 4 pots. In all four pots black glass was present, and the drops of lead were always imbedded in a dark mass of slagged clay. This seems to show that there is a sort of reduction of lead silicate by the iron, forming ferrous silicate and metallic lead. Evidence of corrosion by the lead itself was lacking, since what was observed could be due to the action of iron. Greaves-Walker[1] states that in the reduction of ores in the assay crucible, lead-bearing ores are very corrosive on crucibles high in silica. As the Gross Almerode clay is very silicious, this may account for the opinion commonly expressed by glassmakers that the German clay dissolved rapidly and evenly in the glass (though without throwing stones).

Effect of Iron.—There are two ways in which iron may enter the glass: from the glass batch, and from the pot itself. As to the former, it should be pointed out that iron may enter as the metal itself, introduced purely by accident, it is to be hoped, or as a legitimate mineral constituent of the batch. (This statement applies with equal force to the clay.) As to the former, it may frankly be admitted that under present conditions iron may occasionally be introduced, whether as scale or broken parts from grinding and mixing machinery, carelessness on the part of workmen in leaving nails, knives, bolts, etc., around where they can be swept among the raw materials, or in other ways; and, once in the raw materials, it escapes detection until the pot is broken up. It has been the writer's experience that iron from such sources is far more likely to occur in the glass mix than in the pot clay. In the shaping of the pot, the clay is applied in such thin layers that detection of foreign matter is easy. *The prevention of iron in the glass mix can be accomplished only by screening and magnetic separation at the last possible moment before*

[1] *Trans. Am. Ceram. Soc.*, **12**, 54 (1910).

introduction into the pot. That such precautions are ignored by the majority of glass-houses is an established and deplorable fact.

The percentage of iron as a constituent of the raw materials is of course very low in the case of the soda-ash, niter, sand, red lead and other substances entering into the glass, as compared with the pot clay, which may have an iron content as high as 2 per cent. From a study of the burned clay it is clear that only a small fraction of the iron occurs as a more soluble form (sulphide and oxide), the greater part being combined with the clay, presumably as a complex silicate, and evenly distributed throughout the mass; for the "iron spots" are widely scattered whéreas the clay body is evenly tinged with a buff color. Analyses of the raw clay rarely show traces of sulphur. Now, if a considerable portion of the iron occurred as sulphide or oxide, the inner surface of the walls of the pot would corrode evenly and to a marked degree, and naturally the glass would always show a green color. It is a fact, however, that few spots dissolve markedly in the walls, and, on the other hand, in a number of cases where a considerable volume of clay had been removed from the bottom, there was no trace of anything but clear glass. When masses of clay are torn bodily from the surface and float in the glass as "stones," it always happens that the clay is imbedded in white glass. If iron were to pass into the glass as the clay dissolves, it becomes difficult to explain those cases of marked corrosion where iron is not observed. As the dark glass is always observed at the lowest points of the bottom, it is evidently dense enough to resist being swept upward by the boiling of successive melts. The hypothesis that iron is dissolved out of the clay is not supported by the evidence at hand. The extremely black color of the glass in the fissures, the slagging of the clay around the leak, and the presence of metallic lead all point to the presence of metallic iron, which must have entered in the glass mix.

In the absence of iron, corrosion seems to be a combination of erosion and chemical action. This begins with the formation of superficial crevices, set up probably when the batch is thrown in. As the chemical processes of melting proceed and the gases are evolved, a boiling action develops together with a motion of the glass in currents which sweep over the sides and bottom of

the pot, these currents rising along the back and sides, which are much hotter than the bottom. This motion tears away portions of clay lining the crevices into which the glass has worked, giving rise in time to pitting or honeycombing, which is especially marked in the knuckle. The clay to a great extent passes into the glass or "dissolves," thus doing no harm, or rises to the surface as a scum which can be skimmed off. This is not true in other cases, where the clay remains in the glass as "stones," and the opaque particles are discovered in the finished ware. Solution of the clay in the glass results in the formation of feldspars, and, the glass being normally unsaturated with respect to alumina, the solution may proceed until the bottom of the pot is less than an inch thick, without actual leakage occurring in the worn area. "Stones" may be explained by assuming that the pot has been insufficiently heated in the bottom, which is in a soft-burned or "biscuit" state, and that erosion is very rapid, the fragments passing into the glass being so large that they cannot dissolve in the fining period, or that the glass dissolves some of the clay and then becomes saturated with respect to alumina. All available evidence shows conclusively that soft-burned, porous bottoms corrode excessively, while pots which have been burned to a dense structure offer great resistance to solution. This has been shown in the laboratory by melting a rather corrosive lead glass in 5-inch crucibles, a single melt sufficing to show marked or complete penetration of the bottom of the soft-burned crucibles, while the ones heated to a higher temperature showed a straight, white line of separation between the bottom and the glass. In the present work it was noted that all pots giving 5 melts or less were spongy and a light buff or cream color in the bottom. In fact, it is not possible under present conditions to burn the bottom in the arch to anything like the temperature needed to produce a dense, resistant structure. Travers[1] has shown that this difficulty may be overcome by allowing the pot to remain in the furnace at 1350° C for three days before filling, a solid wall being built up 9 inches in front of the pot, so as to ensure even heating. This practice would do much to remedy conditions in this country, though American glassmakers would undoubtedly object to the

[1] *J. Soc. Glass Tech.*, Sept., **1918**, p. 171.

loss in production such a course would entail. With the idea of heating the bottom to a higher temperature, Jenkinson and Marson[1] have tried supporting the pot in the furnace on fire brick, but found that the bottom warped. At various times, glass-makers have tried burning the inner surface of the pot by introducing a gas- or oil-burner, but this practice was discontinued because it was impossible to spread the heat over a large area.

Sillimanite.—The formation of *sillimanite* ($Al_2O_3.SiO_2$) has been advanced by many investigators in explaining the resistance offered to corrosion by clay which has reached the "vitreous" stage. An exhaustive investigation of the formation of sillimanite and related minerals in glass pots and glass tanks has been made by Wilson,[2] who finds that, normally, sillimanite is developed only in the inner and outer *vitrified* surfaces of the pot, and not to any extent in the bottom. He also states that, with an aluminous clay, the boundary between the glass and the vitrified clay is very sharp, the hard clay surface being full of sillimanite needles, whereas a silicious clay is attacked in an uneven manner, the boundary being irregular and pitted. The life of the pot then depends on the rate of solution of the sillimanite layer; in the former case the glass adjacent to the pot is oversaturated with respect to alumina, whereas in the latter case it is unsaturated. The argument applies with equal force to tank blocks, particularly flux-line blocks. Since the heat inside a tank furnace is never sufficient to vitrify the blocks, it is imperative that all tank blocks be burned to a dense structure in the kiln. Travers[3] points out very clearly that when the clay is vitrified merely by contact with the molten glass, the layer of sillimanite formed is exceedingly thin, whereas that formed in a thoroughly vitrified pot is rather thick. Corrosion in the former case is relatively rapid, especially in the bottom, which is not vitrified by the external heat. Consequently it is useless to vitrify a pot in the manner described above; moreover, it is doubtful whether much is to be gained by lining the pot with aluminous or similar material, because of the danger of such a lining cracking or wearing away in spots, exposing the porous inner clay.

[1] Jenkinson and Marson, *Loc. cit.*

[2] G. V. Wilson, *J. Soc. Glass Tech.*, Sept., **1918**, p. 207.

[3] *Loc. cit.*

Holes.—Concerning the remaining points enumerated above, only a few comments need be made. The question of holes developing in pots is an interesting but puzzling matter. It has been suggested that corrosion begins around a particle of iron (pyrite?), and the glass, having penetrated the surface, easily attacks the less resistant clay beneath. The trouble is one that at times crops up only in isolated cases, at times in a succession of pots, and is on the whole rather a mysterious matter. Of the 22 pots inspected, one had a hole through the side and one a hole through the back. The glass that escaped was clear, and there was no discoloration of the clay around the leak. On the other hand, of 4 pots developing cracks in the side or back, all showed traces of black glass. The theory that holes are due to metallic iron imbedded in the clay would be more impressive if discoloration and slagging of the clay beneath the hole could be detected in every case.

Deformation.—The question of softening and bulging of the pot in the furnace is always important, though, as previously stated, this defect is not usually serious, but occurs when the potmaker is forced, through inability to obtain a raw clay or deterioration of his regular bond clay, to experiment with new material and alter the proportions of raw clay to grog. Certain practices and conditions in glass works are productive of bulging: (1) failure to take down the stopper at the proper moment in the fining period, (2) "forcing" a pot in the hope of remedying stones, color or other defect in the glass, (3) excessive heating of a few pots due to uneven distribution of the heat within the furnace. As a means of judging the resistance to softening, the writer in both routine and experimental work has employed the warpage test, and has found it to be a direct and satisfactory method. The maximum temperature employed in this test was 2700° F., rather than the lower figure of 2500° F., which may be taken as the upper limit for the temperature of the glass. In the light of a previous discussion, it is probable that certain portions of the pot reach a temperature even higher than 2700° F. This surmise is based on the observed color and porosity of pieces taken from the crown and back wall of a number of pots. The porosity is found to increase in the direction of the bottom, which is always

very porous as compared with the "vitrified" portions further up. This condition is very bad, for it aggravates the natural tendency of the glass to corrode the bottom. To correct it, either of two courses may be followed: (1) to burn the bottom to an elevated temperature in the arch or furnace, or (2) to make the bottom of a mixture that becomes dense at a lower temperature.

The former alternative has received some consideration. In regard to the second course, from the writer's experiments and observations of pots recently in use, it appears that there is little to be gained by adding porcelain or similar feldspar mixtures to the pot clay, so long as the pre-heating is not sufficient to bring about a dense structure in the bottom. When pieces of such pots are examined, great fissures are seen extending everywhere through the mass, as though the dense, whitish grains of porcelain had shrunk away from the more refractory matrix. This condition is due to the fact that the different materials were not intimately blended, and is unavoidable when the porcelain is introduced as grog. However, the writer has found that this segregation of the porcelain in the form of white grains occurs even when the raw kaolin, feldspar and flint are individually ground very fine and thoroughly blended with the fire clay. Where such a mixture is in contact with the glass, vitrification extends no further than a depth of about a millimeter, and is not sufficient protection against corrosion because of the rapid solution of the vitrified layer and the danger of a crack exposing the porous material of the interior. Bleininger[1] has recently shown that the porcelain optical glass pot may corrode as much or more than an ordinary pot unless it has been heated to at least 1400° C before introduction of the glass batch.

If the bottom alone were made of a different, denser-burning mixture, trouble would arise from the difference in shrinkage between the bottom and walls, and the possibility of cracking at the knuckle. The fact that bottom-clay is worked stiffer than side-clay would tend to obviate the former, but increase the latter difficulty. Under present working conditions, the walls must not be made less refractory, rather the contrary; moreover, if the pot were as a whole more refractory than it is now, special glasses

[1] *J. Am. Ceram. Soc.*, **1918**, p. 21.

requiring a more elevated working temperature could be melted. All things considered, it is to be hoped that experiments on the use of more refractory substances than fire clays as basic materials in pot construction may be carried out by the intelligent coöperation of pot manufacturers and glassmakers, and that such attempts will lead to gratifying results.

Summary.

1. Examination of the remains of pots used in melting lead glass shows that cracking and corrosion are the chief causes of failure.

2. Cracks are due to strains set up by (1) too rapid heating in the pot arch, (2) insufficient pre-heating, (3) by throwing in the glass batch. The second cause is perhaps the most serious source of trouble.

3. Corrosion is due in some cases to the slagging action of iron on the clay, in most cases to solution of the clay in the fusing alkalies and molten glass. Solution of the clay tends to color the glass, owing to the iron content of the clay, but the tint can be neutralized. Black glass and metallic lead found in pot bottoms are considered to be due to metallic iron in the glass mix.

4. Inability to burn the bottom of the pot in the pot arch accounts for the rapid corrosion of the clay. The trouble might be remedied by allowing the pot to remain empty in the furnace for three days, but glassmakers would object to the loss of production entailed.

5. The vitreous layer formed by heating the inner surface of the pot with an oil-burner, or by the molten glass itself, is very thin, and is not sufficient protection against the attack of the glass. Lining the pot with aluminous or porcelain-like material will not help if there is danger of the lining cracking away (in drying or burning) and exposing the more porous pot clay beneath. The safer method is to burn the pot thoroughly at a temperature of 2500° F., the heat being applied *directly* to the bottom.

6. It appears that little is to be gained by adding porcelain as grog to the pot batch, unless the mixture is rendered dense before use. Moreover, this procedure is objectionable because it would increase the tendency of the walls to bulge.

7. In view of the difficulties attendant upon the use of one clay for the bottom and another for the walls, it seems desirable to search for some material superior to fire clay in refractoriness and in resistance to corrosion.

In conclusion, the writer desires to thank Messrs. Jones, Hess, Barry and Nipper of the Libbey Glass Co. for their kind aid and many valuable suggestions.

CERAMIC LABORATORY,
THE BUCKEYE CLAY POT CO.,
TOLEDO, OHIO.

AN UNUSUAL CAUSE OF SPALLING OF SEWER PIPE.

By Cullen W. Parmelee.

Not long ago the writer was requested to investigate the cause of spalling of sewer pipe which occurred during the burning of the ware. The pipe as it came from the kiln was marred by the flaking of the outside surfaces. Usually these flakes were detached. Sometimes they were almost but not quite separated from the pipe. An examination of the ware showed that in practically every instance a small fragment of what had been a more or less spherical hollow body was imbedded in the detached spall and the other portion of the spheroid was attached to the surface of the fracture of the pipe. These spheroids were about 2 to 3 mm. in diameter. Under a magnifying glass they showed the characteristic appearance of small geodes, that is, small hollow bodies with the interior face of the cavity lined with small crystals. Our opinion regarding the nature of these spheroids was confirmed by members of the faculty of the Department of Geology.

The occurrence of geodes in clay is probably rather unusual but they are known to occur in certain clay deposits in Illinois, notably in the vicinity of Hamilton. These geodes, we are informed by one familiar with that locality, vary in size from a marble to those which are six inches or more in diameter. The larger are more commonly found and do not give rise to trouble except for the expense of repairs to the machinery—due to breakage if these hard nodules are not first removed from the clay.

The spalling, which we observed, accompanied the use of a clay which is of a different character and geological occurrence from that at Hamilton. At the latter place, the geodes are of common occurrence while at the other locality their presence was not known previous to our investigation.

After having determined the probable cause of the trouble, we undertook to locate the stratum containing these nodules. A search of the floor of the clay pit was rewarded by the discovery of a geode imbedded in a large block of a sandstone conglomerate,

which originally had formed part of the rock mass underlying the clay deposit. A painstakingly thorough examination of the rock ledge resulted in the discovery of a number of small geodes varying in size from a hickory nut to a large bean. Together with these geodes was found a remarkable accumulation of more or less perfect quartz crystals, double ended, each not much larger than a kernel of rice. These geodes apparently were located in a very small area on top of the sandstone underlying the clay deposit.

The spalling occurs, apparently, during an early stage of the burning. This is indicated by the small cracks on the reverse side of each spall and radiating from a point almost exactly above the geode fragment—showing that a strain was developed while the clay was at a temperature too low to have given it a permanent set.

The small geodes which we found were all lined with quartz crystals. We are uncertain as to whether the spalling was due to the popping of the geodes—due to the expansion of the air-filled cavities—or whether it was due to the expansion of the quartz particles. Probably the former was the cause.

DEPARTMENT OF CERAMIC ENGINEERING,
UNIVERSITY OF ILLINOIS.

ACTIVITIES OF THE SOCIETY.

January 4, 1918.

Annual Meeting.

Plans are being rapidly formulated for the Annual Meeting, which is to be held in Pittsburgh on February 3, 4, and 5. This will be the twentieth anniversary of the formal organization of the Society, and preparations are being made to commemorate the occasion in fitting manner. Among other things being planned are a banquet, the elevation of a large group of associate members to active membership, the election to life membership of some of the men active in the organization and early development of the Society, and the conferring of Honorary Membership on one or more men whose services in the advancement of ceramic technology has been especially noteworthy. Arrangements are being made to have representatives of allied scientific and technical societies take part in the anniversary program.

This meeting will be of special interest also from the standpoint of the technical and practical worth of the papers and discussions. The forming of Professional Divisions is arousing great interest among the manufacturers and plant executives of the various industries represented on our membership rolls. Papers of interest and practical value to each of these groups are being prepared and arrangements have been made to have these read and discussed in separate sessions of the Professional Divisions. This will give opportunity for free discussion and interchange of views by the men actively engaged in the particular industry represented by the Division. More papers of the kind indicated are earnestly solicited.

A joint session with the United States Potters' Association, many of whose members are aso members of our Society, is being arranged. During the same week, annual meetings will be held in Pittsburgh by the Nationa Brick Manufacturers' Association, the National Paving Brick Manufacturers' Association, the National Building Brick Bureau and the National Clay Machinery

Manufacturers' Association. Opportunity will be given for inspection of the laboratories of the Bureau of Standards and Mellon Institute as well as the unparalleled variety of ceramic plants in the Pittsburgh district.

At the business session several matters of vital importance in the management and development of the Society will come up for decision.

Make your plans now to attend the meeting. It will be the largest, most important, and most enjoyable meeting ever held by the Society. You cannot afford to miss it.

Professional Divisions.

In accord with the motion of Mr. Montgomery reported in Number 8 of the Journal and recently adopted by the Board of Trustees, the President has appointed the following members to act as organization leaders of Professional Divisions.

White-ware and Porcelain	C. L. Sebring
Refractories	A. V. Bleininger
Glass Technology	C. H. Kerr
Abrasives	R. C. Purdy
Enameled Metals	R. D. Landrum
Terra Cotta and Faience	F. B. Ortman
Brick and Tile	M. P. Blair

Members are urgently requested not to wait for an appeal from the leaders, but to become actively interested themselves and to arouse the interest of every ceramic man they know in the organization of one of these Divisions.

Nominations for Active Membership.

The Board of Trustees desires that members send to any member of the Board at once nominations for active membership. Many of our associate members deserve this elevation, and it is desirable that the voting power in the Society be more widely distributed. It is to be noted that the presentation of papers is no longer the sole basis for elevation to active membership. Following are extracts from the revised rules of the Society covering this subject:

"Active members must be persons competent to fill responsible positions in ceramics. Only associate members shall be eligible to election as active

members and such elections shall occur only in recognition of attainments or of service in the science, technology, or art, of the silicate industries."

"To be promoted to active membership associate members must be nominated in writing by an active member, seconded by not less than two other active members, and approved by the Board of Trustees. Their nomination must be accompanied by a statement of their qualifications and to be elected they must receive an affirmative vote of the majority of the members of the Board of Trustees."

Honorary Secretaryship.

DECEMBER 22, 1918.

MR. HOMER F. STALEY,
Bureau of Standards,
Washington, D. C.

MY DEAR STALEY:

I am in receipt of your message to the effect that the American Ceramic Society desires to create a new office, that of Honorary Secretary, and to elect me to it. I am, of course, not insensible to the honor which the Society desires to confer upon me, and greatly value this added proof of their good will. Nevertheless, I must refuse it.

The custom of having Honorary officers is common and well established in English and European Societies, but here it is rather anomalous. In England, the Honorary officers have little part in the actual achievements of the organization, the work being done by the active officers, but the position fills a useful purpose nevertheless, as there are always members of the upper class whom it is desirable to recognize.

I should be loath to see this custom, which belongs to a social structure quite different from ours, become popular in the United States, and still more unwilling to see myself figuring in such a capacity. When the exigencies of the war are ended, if I find that I can take up the threads of my former life again, the only status I should care to have in the Society would be that of an active worker, where I could mingle on terms of exact equality with everybody, and where I would be unhampered in making any views and purposes felt.

I feel sure that you can make the Society see, after they have given the matter a little more deliberate consideration, that the course which I propose is really the safe and democratic one and is for their best interests.

With kindest personal regards,

(Signed) EDWARD ORTON, JR.,
LIEUT.-COLONEL, M. T. C.,
UNITED STATES ARMY.

The Journal of the American Ceramic Society

THIS JOURNAL, the official organ of the American Ceramic Society, appears at this time to fill a need of the American Ceramic Industries.

It is to be published monthly, and for this reason embraces a wider field of activity than the volumes of the Transactions which it succeeds, and thereby offers greater opportunities of service to Ceramic Science and Industry.

The success of this Journal will depend upon the efforts of the individual members. Your contributions, your discussions and your suggestions, are necessary; but above all, your assistance in securing new members for the Society and subscribers to the Journal is of prime importance. The Committee on Publications therefore requests that each member of the Society be personally responsible for securing all possible members and subscriptions in his own city or town.

The subscription price is—$6.00 per year to non-members.

The annual membership dues of the Society, five dollars per year, include subscription to the Journal.

The public library, the librarians of the nearby universities, colleges or other institutions, as well as individuals who are, or ought to be, interested in the work of your Society are your objectives.

Use the application blanks at the bottom of this sheet for enrolling members and subscribers. Applications should be mailed to Prof. Charles F. Binns, Alfred, N. Y.

Complete and energetic support on the part of the membership will insure a conspicuous success for our new publication.

COMMITTEE ON PUBLICATIONS.

Application for Membership in the American Ceramic Society

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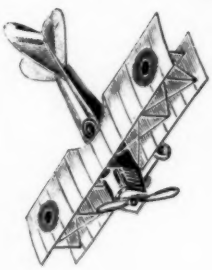

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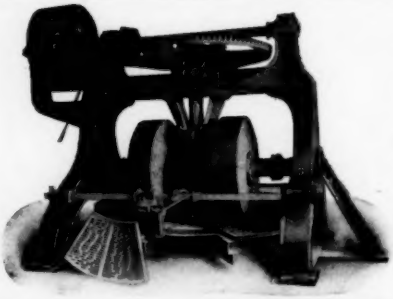

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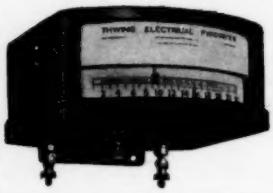

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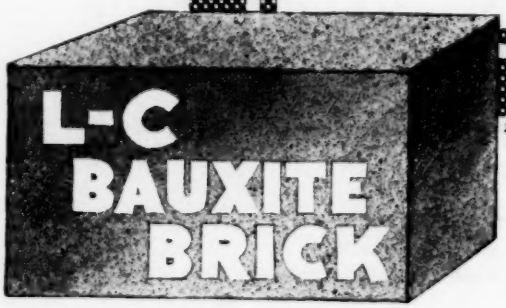

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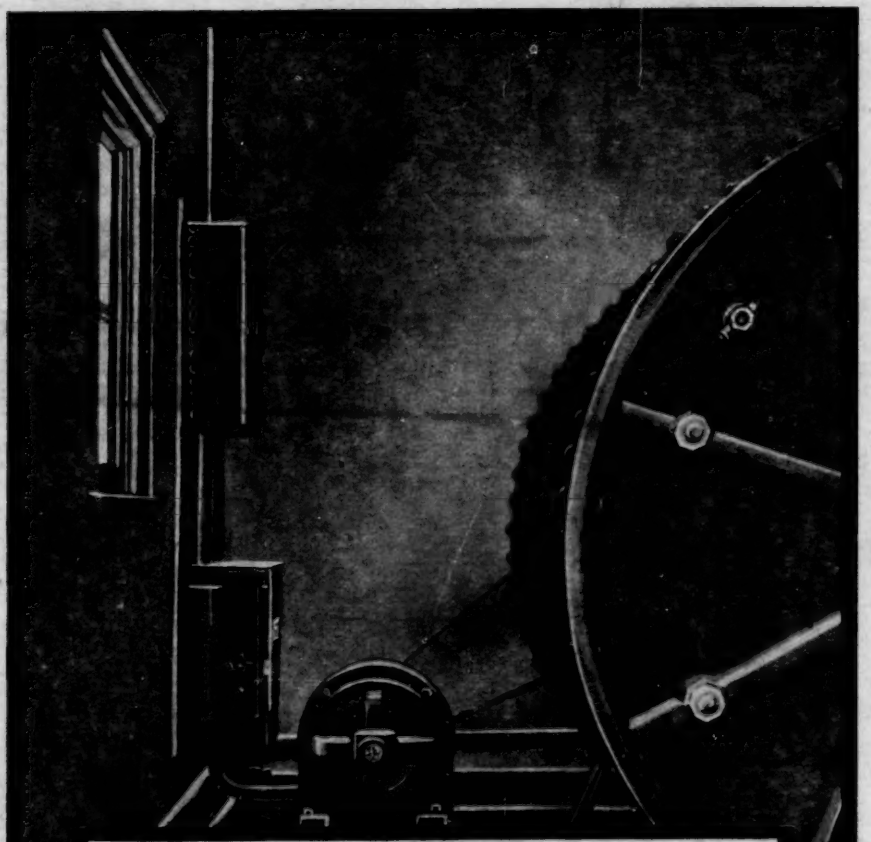

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